THE PERFORMANCE OF SILICON BASED SENSOR AND ITS APPLICATION IN SILVER TOXICITY STUDIES

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The silicon based sensor is able to detect part per trillion ionic silver in 0.0098% hydrofluoric acid based on the open circuit potential (OCP) measurement. The OCP jump of 100 ppt ionic silver solution is up to 120 mV. The complex agent can effectively suppress the ionic silver concentration and suppress the OCP signal. The ability of complex agent to suppress the OCP signal depends on the formation constant of the complex with silver. The complex adsorbed on the sensor surface induces a second OCP jump, the height of the second jump depends on the formation constant of the complex. The MINEQL chemical equilibrium modeling program is used to calculate the ionic silver concentration when complex agent presents, a discrepancy is found between the MINEQL simulation result and the OCP signal of the silicon based sensor. The toxicity of ionic silver to C. dubia is studied parallel to the OCP signal of silicon based sensor. Less toxicity is found when the complex agent is present similar to the OCP signal. Another discrepancy is found between the MINEQL simulation and the toxicity test when MINEQL simulation is used to predict and control the ionic silver concentration. The data from both biosensor C. dubia and silicon based sensor support each other and both are not in agreement with MINEQL simulation prediction.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

SCHEME

CHAPTER 1

INTRODUCTION

The chemistry of silicon has been studied extensively due to its unique properties and applications in microelectronic industry. Recently silicon based sensor has been demonstrated to be a versatile sensor with both academic significance and industrial applications. The application of silicon based sensor in the monitoring of ultratrace metallic and organic contaminants in the semiconductor production process has been explored by O. M.R. Chyan et al successfully.[1],[2],[3],[[4] The ability of silicon based sensor to detect trace metallic contaminants in hydrofluoric acid and trace iron in hydrogen peroxide based on direct open circuit potential (OCP) measurement combined with the Atomic Force Microscopy (AFM) were reported.[1], [2] Another approach of this sensor based on Multiple Internal Reflection Infrared Spectroscopy (MIRIS) is studied, wherein an IR beam is directed to travel through silicon sensor crystal and undergo multiple internal reflections, the evanescent wave due to the interference of incoming and outgoing wave can effectively detect the trace level of organic contamination in hydrofluoric acid,[4] this method offers a means to monitor the organic contaminants in the etching process of silicon production.

Recently, more advances were made by O. M. R. Chyan's research group, the possibility of this measurement to monitor the quality of the ultrapure water in research lab and industry is reported.[3] The data shows that the silicon based sensor has more acute response than the sensor used in the Millipore water unit. A silicon based IR sensor was

also developed for environmental applications. The silicon sensor is coated uniformly by Nafion/Dimethylglyoxime(DMG) mixture. The Nickel ion, which has environmental significance, will interact with the coating and the chemical bonding is changed, this signal is detected by IR sensor. 1-5 ppm Nickel ion can be detected in the pH range 6-8.[5]

In this work, we concentrate on the performance of the silicon based sensor in silver containing solutions, and obtain a calibration curve for this sensor. We use certain complex anion species to precipitate and complex the silver to reduce the ionic silver concentration and measure the OCP jump of our silicon based sensor. We use the MINEQL chemical equilibrium modeling program to calculate the ionic silver ion concentration, and compare the silicon sensor OCP jumps of silver solutions with and without complex species when the ionic silver ion concentrations are supposed to be the same based on the MINEQL simulation.

When precipitation and complex species are used in our studies, we found out that the aqueous silver precipitation or complex in the solution might attach on the surface of the sensor. When the sensor is transferred to fresh 0.0098% HF solution without the complex agent, those species attached on the sensor will decompose and the free silver ions come out to cause the second OCP jump. It is noticed the height of the second OCP jump is related to the abilities of the precipitation and complex anions to bind with the silver ion.

Based on it's excellent ability to detect low level silver and tell the difference from complex and precipitate, we also focus on the application of the silicon based sensor in the silver toxicology studies. Silver (Ag) is a trace metal that has wide spread uses in society.[6,7] Silver concentration in urban surface are found to be 10-100 ng/L compared with about 5 ng/L in rural area.[8] Silver (I) is concentrated in the solids fractions of the sludge and sediment associated with the municipal wastewater treatment.[9] Rozan et al suggested that the industrial use of silver during the 100 years led to the Ag(I) accumulation in stream sediment in urban areas.[10] Most silver(Ag) in surface water originates from natural leaching, it is believed that elevated concentrations are normally related with industrial activities such as mining and photographic processing. [11] In recent years, Silver (Ag) recovery from photoprocessing effluent has become increasingly more efficient because of environmental awareness and economic demand for silver.[12] Total silver concentrations discharged from photographic processing are in the low ppm level, most of them are associated with thiosulfate. The effluents discharged from photoprocessing are supposed to be substantially diluted with other sewage then go through the treatment plants which typically reclaim up to 94% Silver.[9] After the treatment in waste water treatment plants, the discharged total silver to the environment varies from picogram per liter to low microgram per liter level, while the natural background concentrations are in the low nanogram per liter range. Most of them are bound to particles, organic colloids, thiosulfate, sulfide, dissolved organic matter, and chloride.

The United States government started to protect environment resources almost 100 years ago. Silver, along with other metals and organic materials, was regulated since the early 1960s.[13] The United States Public Health Service originally included silver in it's drinking water standards, according to the standards, the maximum silver allowed in drinking water was 0.05 mg/L.[14] In late 1990s, the Environmental Protection Agency (EPA) of the United States set up the regulations controlling silver in the work place and environment.[13] The maximum concentration allowed in drinking water is 0.1mg/L, in work places it is 0.01mg/m^3.

Ionic silver is one of most toxic anthropogenic metals, although it poses little health risk to human beings.[15] Acutely toxic free ionic silver in natural system is not found, however, silver complexes are dominant in effluent and other sources. And these complexes are not so harmful to biotic and abiotic process because they are much less toxic than ionic free silver.[16] It is clearly demonstrated that speciation is extremely important in evaluating the silver's direct toxic effects. Complex species that keeps the silver in bound state do not generate a toxic response.[17] It is reported that the competitions occurred between silver and several aqueous species that are able to bind the ionic silver, the bioavailabity is decreased and moribund physiological response is decreased, too.[16]

In this work, we use the water flee(Ceriodaphnia dubia) as a biosensor to observe the its survival rate in various concentrations of ionic silver solutions. We also observe the survival rate improvement when complex agent is used to lower the ionic silver

concentrations in solutions. We use both silicon based sensor and MINEQL chemical equilibrium modeling program to predict the ionic silver concentrations and try to correlate the survival rate of C. dubia with the calculated ionic silver concentrations. We successfully correlate the toxicity of the silver with complex solutions based on the C. dubia survival rate with the silicon sensor OCP signal in silver solutions with different complex anion concentrations.

CHAPTER 2

SILICON SENSOR AND ITS PERFORMANCE

2.1 Introduction

A novel silicon based sensor able to detect trace metallic contaminants in hydrofluoric acid and the trace iron in hydrogen peroxide is developed and reported.[1],[2] ,[18] Its principle is based on the direct measurements of the open circuit potential (OCP) jump of the silicon based sensor, the OCP jump is from the charge transfer reaction between metallic ions in HF solutions and the silicon sensor surface. Highly oxidized noble metal ions such as Ag^{+}, Cu^{2+}, Au^{3+}, Pt^{2+}, and Pd^{2+} can be reduced and deposit on the silicon sensor surface and silicon is oxidized. The copper deposition on silicon surface is studied and reported by O. M.R. Chyan et al.[19] The metal deposition results in microscopic metal/semiconductor Schottky barrier that induces a positive band bending in the silicon space charge region. [20], [25] The silicon oxidation and Schokky barrier enable the silicon based sensor to achieve down to part per trillion sensitivity.

The OCP jump can be easily measured with usual pH/ion meter and the sensor can be made directly from commercially available n-type or p-type doped silicon wafer, double junction Ag^{+}/AgCl reference electrode can be chosen to be the reference electrode. These three items make the whole experiment setup. A very low cost is required but it achieves low part per trillion (ppt) to part per billion (ppb) sensitivity. This methodology is practical for the contamination monitoring in microelectronics industry where the on-line

monitoring ultra-trace metallic and organic contamination is so desirable. Hydrofluoric acid is used in all solutions to maintain the hydrogen termination of the silicon sensor all the time, and to avoid the formation of oxide layer. It is reported that the hydrogen termination is quite inert to the air oxidation, but when water is involved it facilitate the oxidation of the silicon. [21] The 0.0098% HF has been used by previous workers and it has been turned out to be good system for this methodology.

In this chapter, we measure the OCP jumps of series ionic silver in 0.0098% HF solutions and get calibration curve from 25 ppt to 10 ppb ionic silver solutions. We also study the amount of metal deposition on the silicon sensor by successive twice OCP measurements on the same solution. Complex anion can lower the anionic silver concentration by binding to silver and form complex. Its ability to lower the ionic silver concentration depends on the complex formation constants. We use different complex anions to lower the silver concentration and observe the suppressed OCP jumps as we expect. We also find out that the complex species can stay on the surface of the sensor, when we transfer the sensor to fresh 0.0098% HF solution, we observe a second OCP jump, which we believe is due to the decomposition of the complex species on the silicon sensor. The height of the second jump is studied by using different complex anions and it turns out that the height of the second jump is complex stability dependent. The second OCP jump can be easily totally suppressed by transferring to sensor to 0.0098% HF with complex anions. In order to calculate the ionic silver concentration in the solutions with complex agent, we use MINEQL chemical equilibrium modeling software to simulate the

distribution of all the species especially the ionic silver down the ppb and ppt level and compare the simulation results with the silicon sensor OCP measurement results.

2.2 Experiment

2.2.1 The fabrication of silicon based sensor and its pretreatment

The silicon chip is made by cutting <111> n-type Arsenic doped CZ silicon wafer into 2 cm x 0.5 cm chip using diamond tip scriber along its crystal boundary. Before every OCP measurement, the chip needs pretreatment that is designed to clean the chip surface and make the surface oxide free. The pretreatment process includes SC1 and SC2 cleaning.

SC1 cleaning is a process of boiling the chip in SC1 solution (5:1:1 = H_2O : H_2O_2 : NH_4OH) for 15 minutes, which is supposed to effectively removed absorbed organic contaminants from the silicon surface.[22] After SC1, the chip is etched in 4.9% HF for 10 minutes to remove the oxide film formed in SC1 boiling. This etching is followed by SC2 cleaning. SC2 cleaning is a process of boiling the silicon chip in SC2 solution (5:1:1= H_2O : H_2O_2 : HCl) for 15 minutes. This process is supposed to remove the absorbed metallic contaminants on the silicon surface. The silicon chip is etched in 4.9% HF for 10 minutes again after SC2 cleaning to remove to oxide film formed in SC2 cleaning. Then the chip is rinsed with ultra pure water and purged to dry by nitrogen flow and ready for use.

2.2.2 Equipment and chemicals

The open circuit potential (OCP) of the silicon sensor is measured with respect to the Ag^+/AgCl double junction reference electrode (Orion, model 900200), outer solution is 10% KNO_3 solution. This reference electrode has been proved to be stable for 8 hours in our experiments. The open circuit potential is measured by high input impedance potentiometer(Accumet 50, Fisher Scientific) . All kinds of hydrofluoric acid solutions are diluted from high purity 49% HF (electronic grade, Hashimoto, Japan), all solutions are prepared and contained in custom-made perfluoroalkoxy polymer(PFA) beakers, all the beakers are boiled 3 times in 10% nitric acid before use, each time 2 hours long. And they are finally rinsed by ultra pure water (Resistance >18.2 M Ω). The water is obtained by Millipore Q UV Plus water unit. The Ag^+ solution is verified by Inductively Couple Plasma-Mass Spectroscopy (ICP/MS, Fisons Model PQS) independently, NaCl, NaBr, $Na_2S_2O_3$ and KCN reagent are purchased from Aldrich Chemical.

Apart from the plunger setup we reported before, we developed a clip setup that both sides of the silicon chip are exposed to solutions, the clip is made from normal clip and conductive epoxy and golden film. One end of the silicon chip is clipped by the clip and the other end of the silicon chip is immersed into solution. The clip configuration and the experiment set up are showed in Figure 2.1 and Figure 2.2:

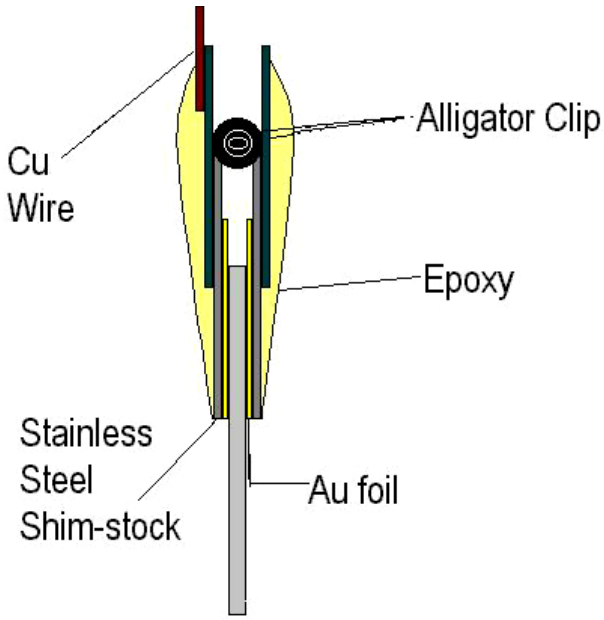


Figure 2.1: The clip setup

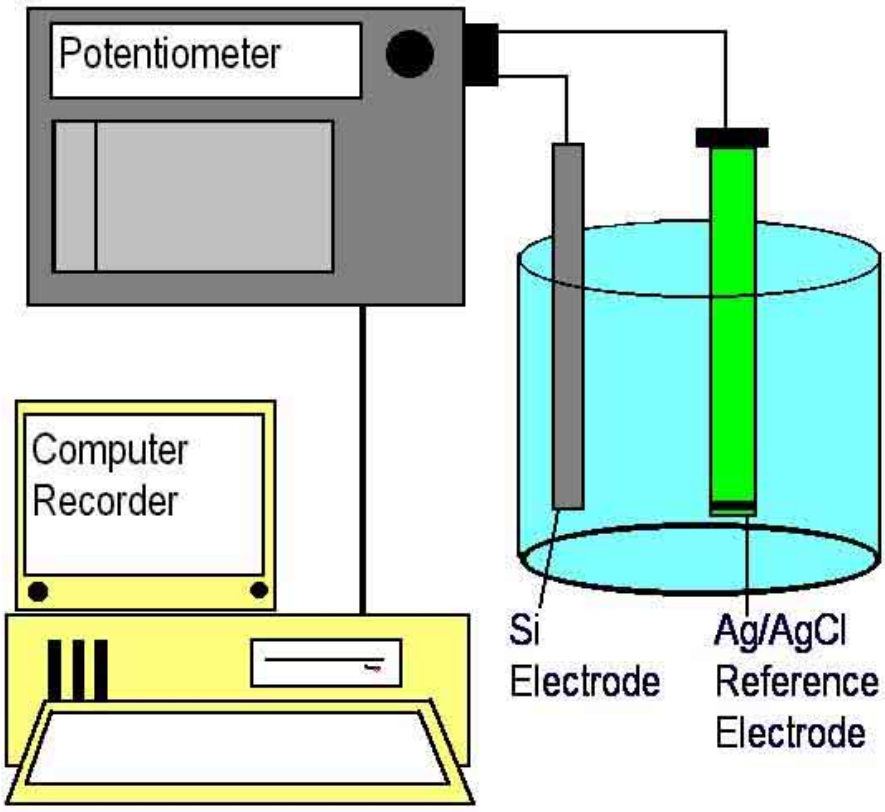


Figure 2.2: Open circuit potential measurement setup

2.3 Results and discussions

In our previous works, we used the sensor with plunger setup to detect trace iron, copper silver in 0.0098% HF solution.[1],[2] In the plunger setup, the silicon electrode has a backside contact and only the front side of the silicon chip is exposed to the solution. Experiments have been done to show that the exposed area doesn't alter the potential result. In this work we develop a new clip setup which works more conveniently but same efficiency for trace metal detection. In this clip setup, one end of the sensor is clipped and the other end is immersed into the solution, both sides and the edge of the silicon sensor are exposed to the solution. The area exposed to solutions can be controlled by adjusting the depth of the immersion of the Silicon sensor. Little difference is observed between the 0.5 cm immersion and 1 cm immersion of the silicon sensor.

2.3.1 The calibration curve of standard silver solutions

Figure 2.3 shows the silicon based sensor OCP measurement of the silicon sensor in 100 ppt Ag^+ solution. The first 30 minutes running in 0.0098 % HF works as baseline and at the end of the 30 minutes, the base line is stable at -526.7mV. The chemical reactions at the silicon sensor are the hydrogen evolution and the dynamic HF etching. After baseline is attained the sensor is transferred to 100 ppt Ag^+ in 0.0098% HF. Ag^+ ions are reduced to Ag metal and deposit on the surface of the Silicon sensor.

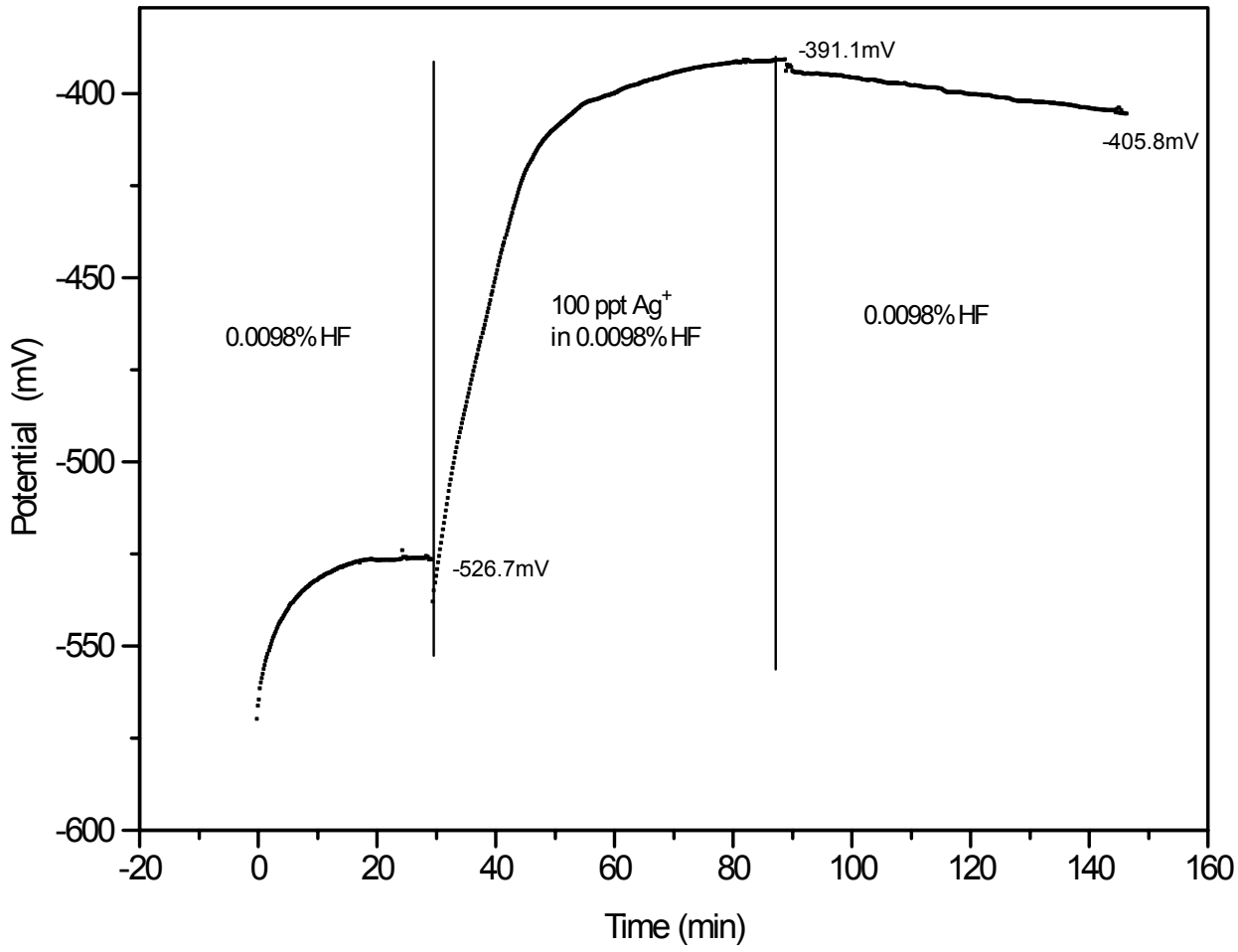


Figure 2.3: Open circuit potential measurement of

100 ppt Ag^+ in 0.00098% HF

$$4Ag^{+} + Si + 6HF \Rightarrow 4\,Ag + SiF_6^{2-} + 6H^{+} \qquad \text{Equation 2.1}$$

The highly energetically favorable Ag^{+}/ Si reaction can extract surface electrons from silicon chip and the open circuit potential shifts to more positive values.[23] After 1 hour running in 100 ppt Ag^{+} in 0.0098% HF the potential is stable at -391.1mV. It is transferred back to the 0.0098% HF, the potential drops slightly and become stable at -405.3 mV. This drop is due to the loss of the Ag metal deposition on the silicon sensor surface when it is physically moved from one solution to another solution. That the open circuit potential doesn't drop to it's baseline value proves that the OCP jump is mainly from the Schokky barrier.

The same measurements are performed from 50 ppt Ag^{+} to 10 ppb Ag^{+} in 0.0098% HF solutions and a calibration curve is made. This method is low concentration sensitive, when the concentration reaches high part per billion (ppb) range, the curve is compressed and straight line is not available. This is because when the concentration reaches high part per billion leve r, the silver deposition on the silicon surface is saturated, increasing the Ag^{+} concentration in solution is not able to enhance the Schokky barrier which is a major factor contributing to the OCP jump. Figure 2.4 shows the calibration curve.

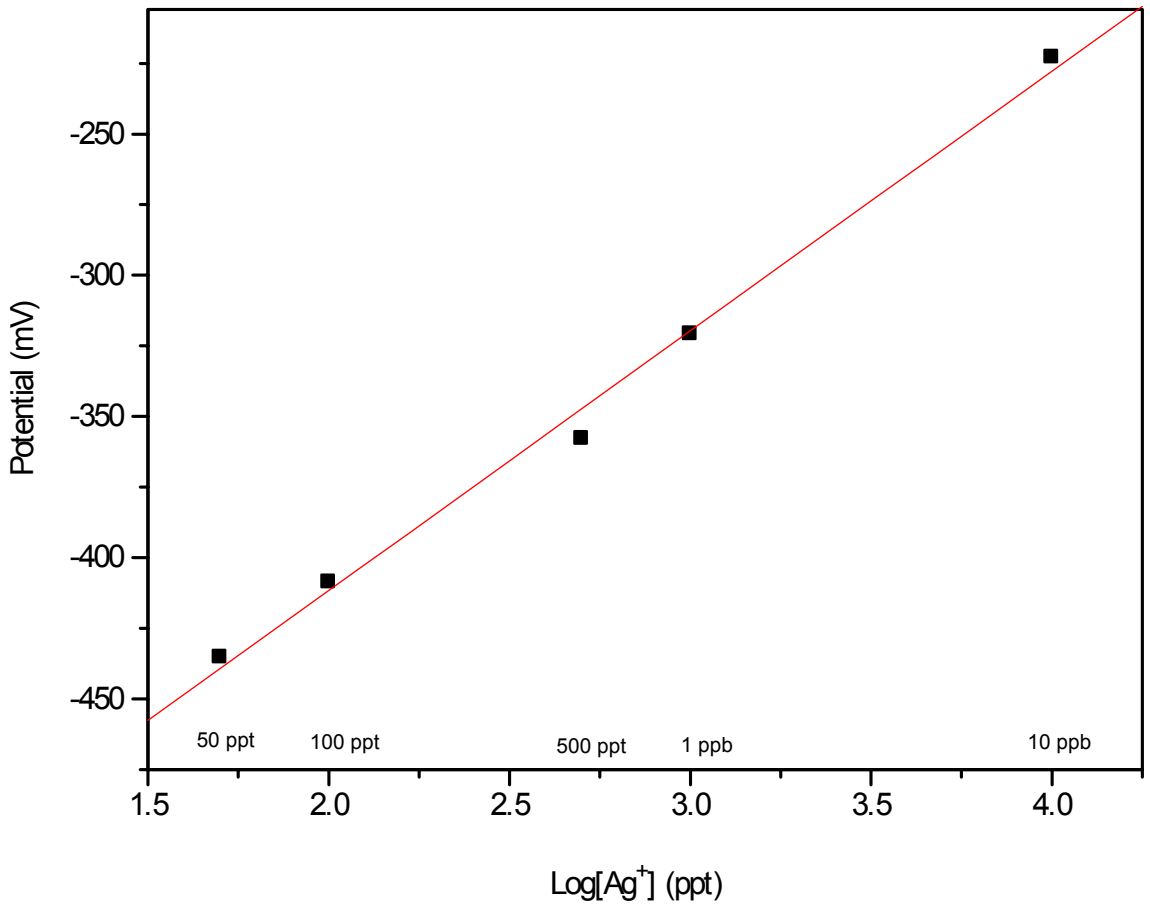


Figure 2.4: Calibration curve of Ag^+ in 0.0098% HF solution based on open circuit potential measurements

2.3.2 Amount of Ag^+ deposition

When we do the OCP measurement at 100 ppt Ag^+ in 0.0098% HF solution as Figure 2.5 shows, we understand the silver deposition occurs and the solution lose some Ag^+ ions. Since the Ag^+ concentration is so low, the best way to know the amount of Ag^+ deposition on the surface is to perform the OCP measurements twice successively on a same 100 ppt Ag^+ in 0.0098% HF solution. Figure 2.5 shows such an experiment. It is found out that the first time and the second time OCP measurements have very close potential jumps. It indicates that very small amount of Ag^+ is removed from the solution and deposit on the surface of the sensor. The sample after being analyzed by this method has the same concentration as the original sample does. This will make the sample be able to repeatedly measured.

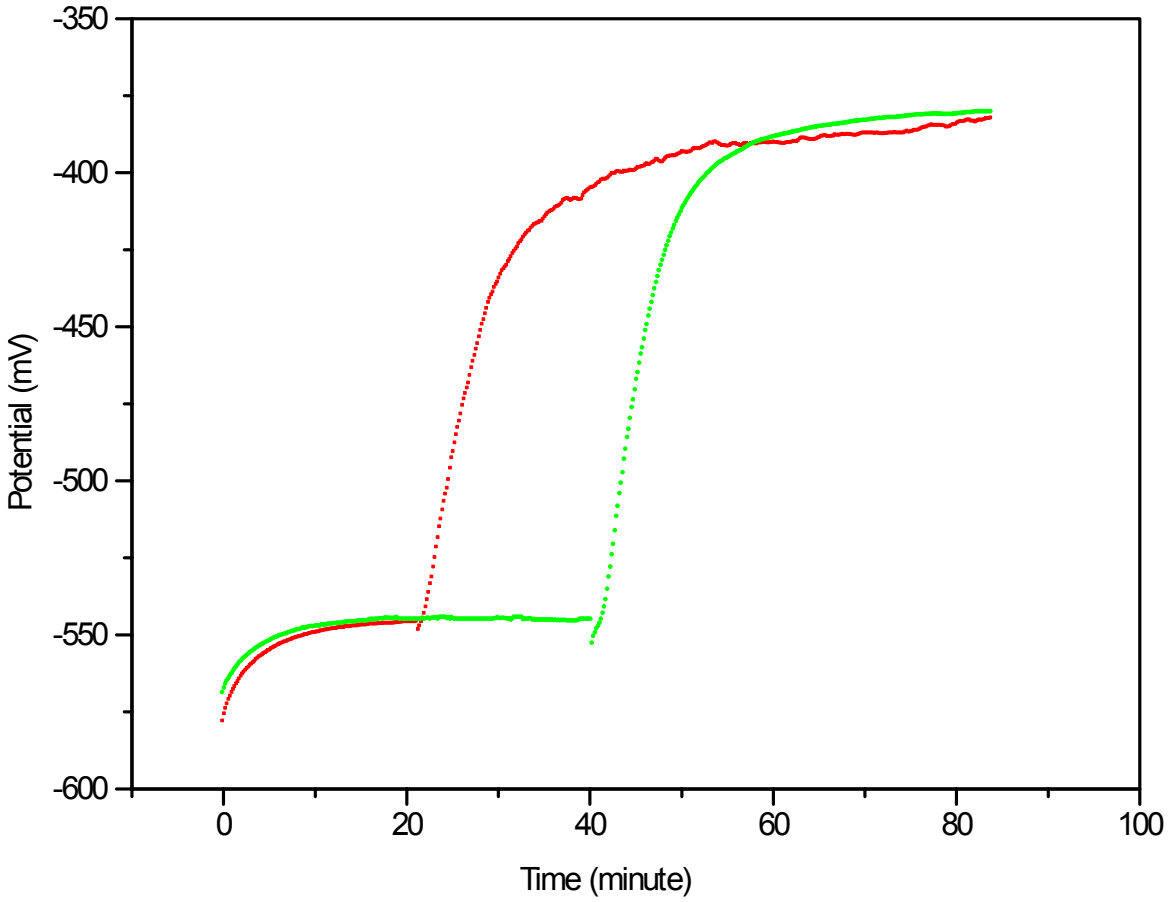


Figure 2. 5: Successive twice open circuit measurements of 100 ppt Ag^+ in 0.0098 %HF

2.3.3 Complex anions effect and second jump

2.3.3.1 The complex anion effect

It is expected that the complex anion will effectively decrease the ionic silver in silver solution, correspondingly the signal from the OCP measurement of the silicon based sensor will decrease. The OCP measurement of 5 ppb Ag^+ in 0.0098 %HF is showed in Figure 2.6.

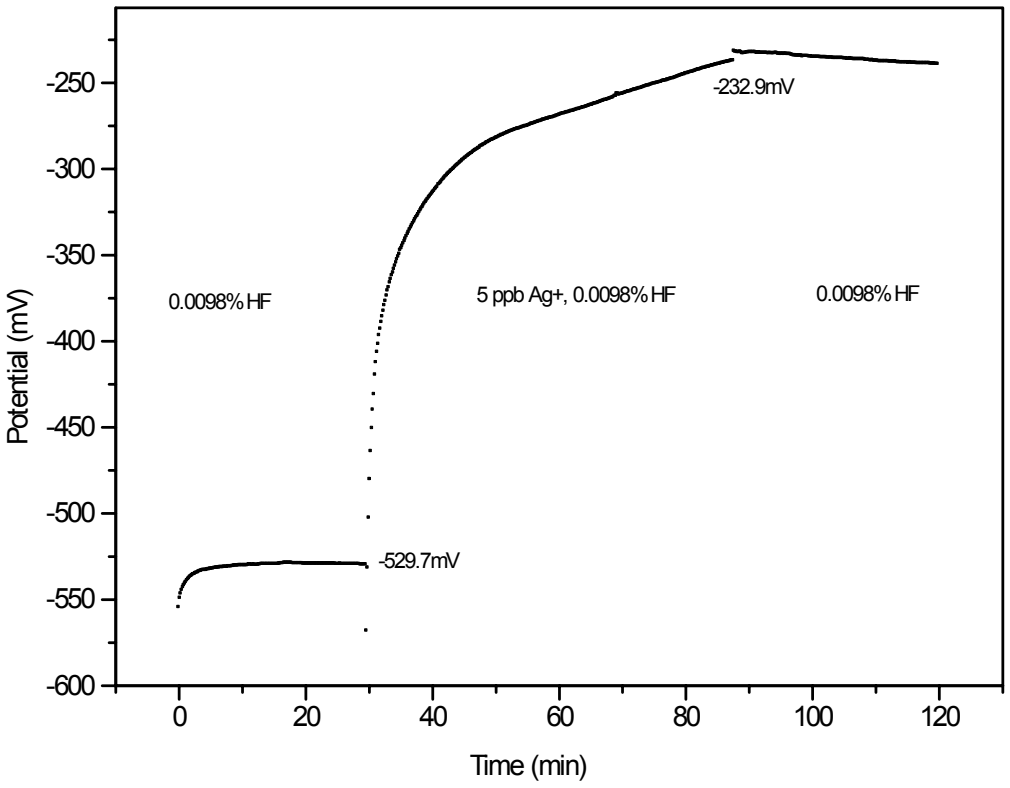


Figure 2.6: The OCP measurement of 5 ppb Ag^+ in 0.0098% HF

In order to see the difference between the ability of the complex anion to bind with ionic silver 0.1 M NaCl and 0.1 M $Na_2S_2O_3$ are used to react with 5 ppb Ag^+ in 0.0098 % HF. Figure 2.7 shows the OCP measurements of both solutions.

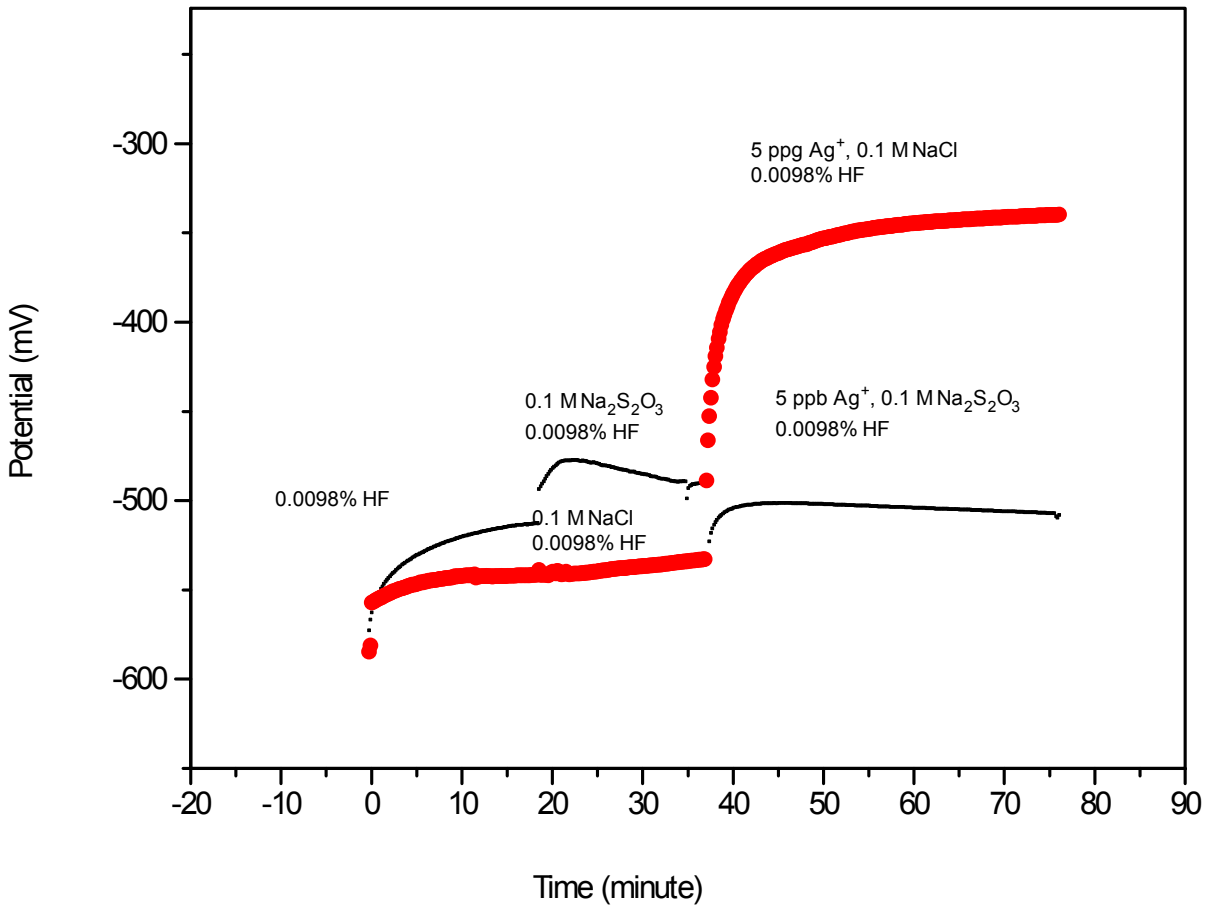


Figure 2.7: The open circuit potential measurement of 5 ppb Ag^+, 0.1 M NaCl and 0.1 M $Na_2S_2O_3$ in 0.0098% HF solutions

As Figure 2.7 shows, the OCP measurement signals are effectively suppressed in the complex 0.1 M Cl^-, and $S_2O_3^{2-}$ solutions. This indicates the ionic silver concentrations in the solutions are decreased by the complex anion Cl^- and $S_2O_3^{2-}$.

$$Ag^{+} + xCl^{-} = AgCl_x^{1-x} \qquad \text{Equation 2.2}$$

$$Ag^{+} + xS_2O_3^{2-} = Ag(S_2O_3)_x^{1-2x} \qquad \text{Equation 2.3}$$

In addition, Cl^- and $S_2O_3^{2-}$ have different abilities to bind with ionic silver, the formation constants of $AgCl_x^{1-x}$ and $Ag(S_2O_3)_x^{1-2x}$ are listed in Table1, it is obvious that $S_2O_3^{2-}$ ion has higher formation constants and it decrease the ionic silver more effectively. The OCP jump of 5 ppb Ag^+ is decreased down to -339.4mV by 0.1 M Cl^-, as a comparison, 0.1 M $S_2O_3^{2-}$ is able to totally suppress the OCP jump of 5 ppb Ag^+ in 0.0098% HF solution.

2.3.3.2 The discrepancy between OCP measurement and MINEQL simulation

The MINEQL chemical equilibrium modeling software is developed by Environmental Research Software(ERS) for water chemistry calculations.[29] Its calculation is based on the thermodynamic data of all the related chemical species. Calculations can be performed at moderate temperature (0~50 degree centigrade) and moderate ionic strength. It enables us to calculate the distribution of all species of the silver with complex anion solution. Since we already have the calibration curve for ionic silver solution without any complex, we do the silicon sensor OCP measurement on the silver with complex anion solutions and compare its OCP jump with the silver solutions without complex anion but both solutions are supposed to have equivalent ionic silver concentrations based on MINEQL and solution preparations.

Figure 2.8 shows the MINEQL simulation of the distribution of all species of the 5 ppb Ag^+ with 0.014 M NaCl in 0.0098% HF solution.

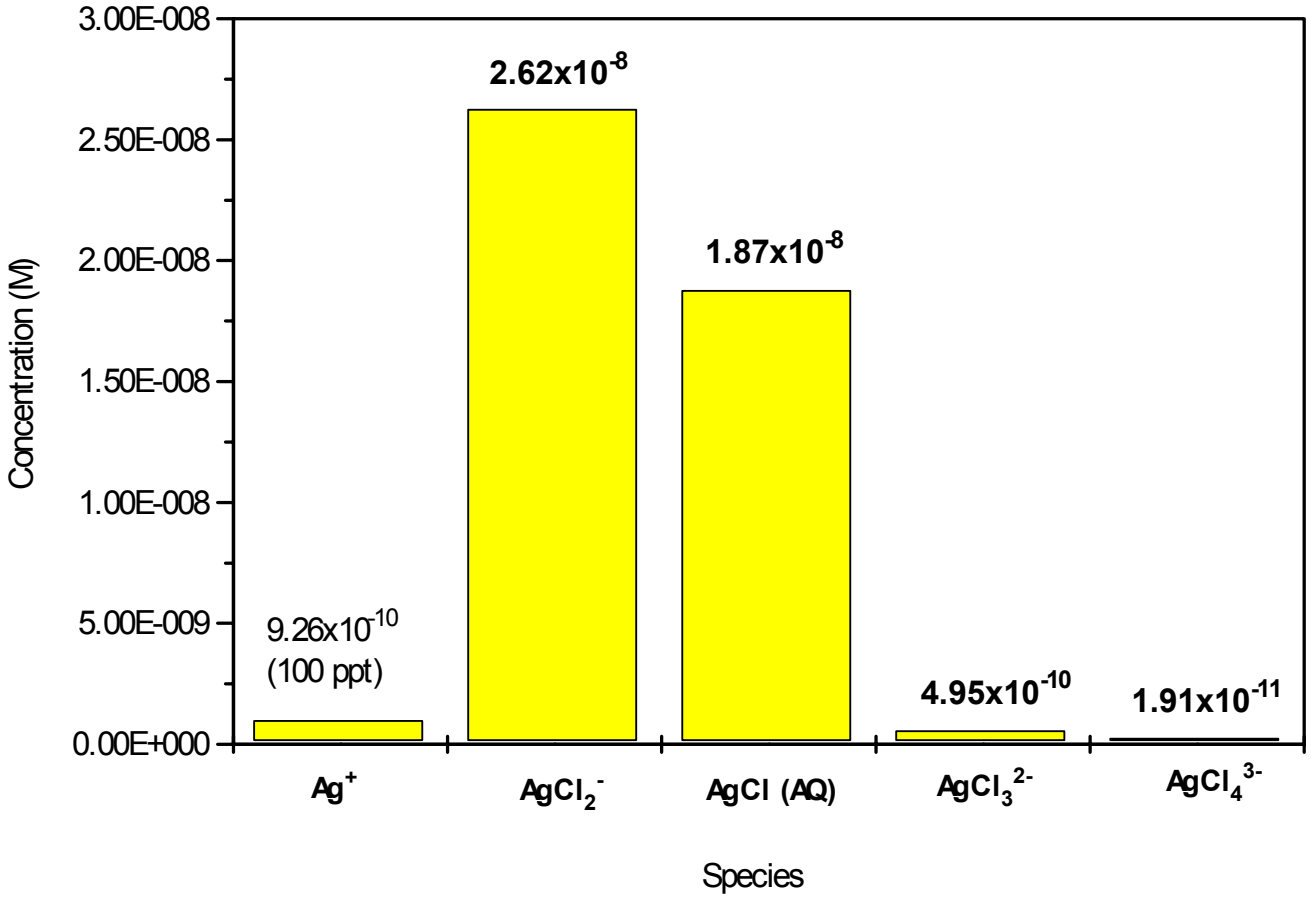


Figure 2. 8: MINEQL simulation of 5 ppb Ag^+ with 0.014 M NaCl in 0.0098%HF

The simulation result shows that the ionic silver in 5 ppb Ag^+ with 0.014 M NaCl solution is 100 ppt. OCP is measured on this solution and the potential jump is –289.1

mV as Figure 2.9 shows. This value is much higher than the value of 100 ppt Ag^+ in 0.0098% HF that should be at about –400 mV based on the calibration curve.

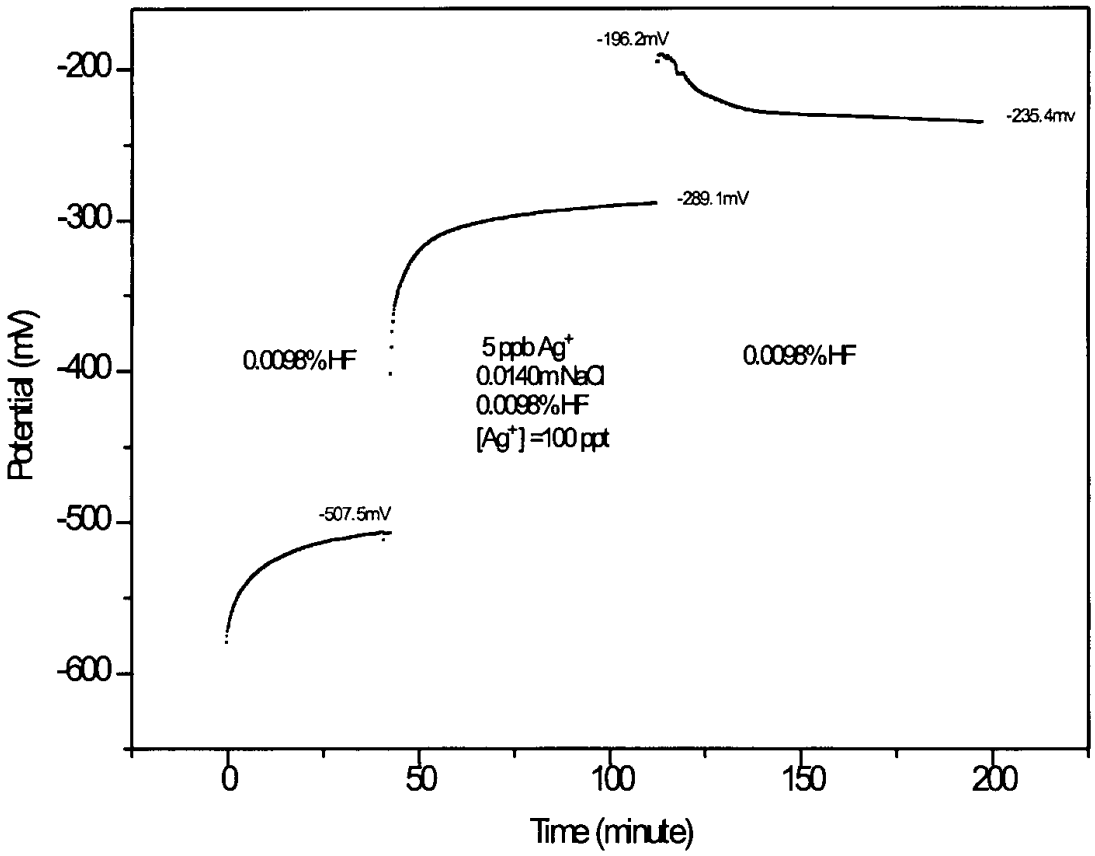


Figure 2.9: Open circuit potential measurement of 5 ppb Ag^+ with 0.014 M NaCl in 0.0098% HF

The results indicate that the simulation doesn't work correctly in the low concentration range such as ppt range, the real concentration of the ionic species is higher than the

simulation result. Other complexes including Br^- and $S_2O_3^{2-}$ are used and the similar phenomenon is observed. And this conclusion is reconfirmed in the biosensor water flee (C. dubia) toxicity experiments in chapter 3.

2.3.3.3 The second jump in transfer and its elimination, height and concentration relationship

At the end of the OCP measurement of the silver complex in 0.0098% HF solution, the sensor is transferred to fresh 0.0098% HF solution. A second potential jump is observed as Figure 2.9 shows. We hypothesize that this second jump is due to the complex species in the solution. The complex species are absorbed on the surface of the silicon sensor when the metal deposition is happening. These complexes will decompose (Equation 2.4) and ionic silver will come out when the sensor is transferred to fresh 0.0098 % HF. Although the amount of outcoming ionic silver is small, but they are close to the surface of the sensor and easy to extract electron from silicon and get reduced, the silver deposition happens and causes the second jump.

$$AgCl_x^{1-x} \Rightarrow Ag^+ + xCl^- \qquad \text{Equation 2.4}$$

$$4\,Ag^+ + Si + 6HF = 4Ag + SiF6^{2-} + 6H^+ \qquad \text{Equation 2.1}$$

The decomposition reaction can be effectively inhibited, i.e. elimination of second jump, if the sensor is transferred to 0.0098% HF solution with complex ion and the second jump can be suppressed. This complex ion effect on the second jump is shown in Figure 2.10.

The complex ion effect in inhibiting the second jump is also observed in Br^-, $S_2O_3^{2-}$ ion solutions and other concentrations.

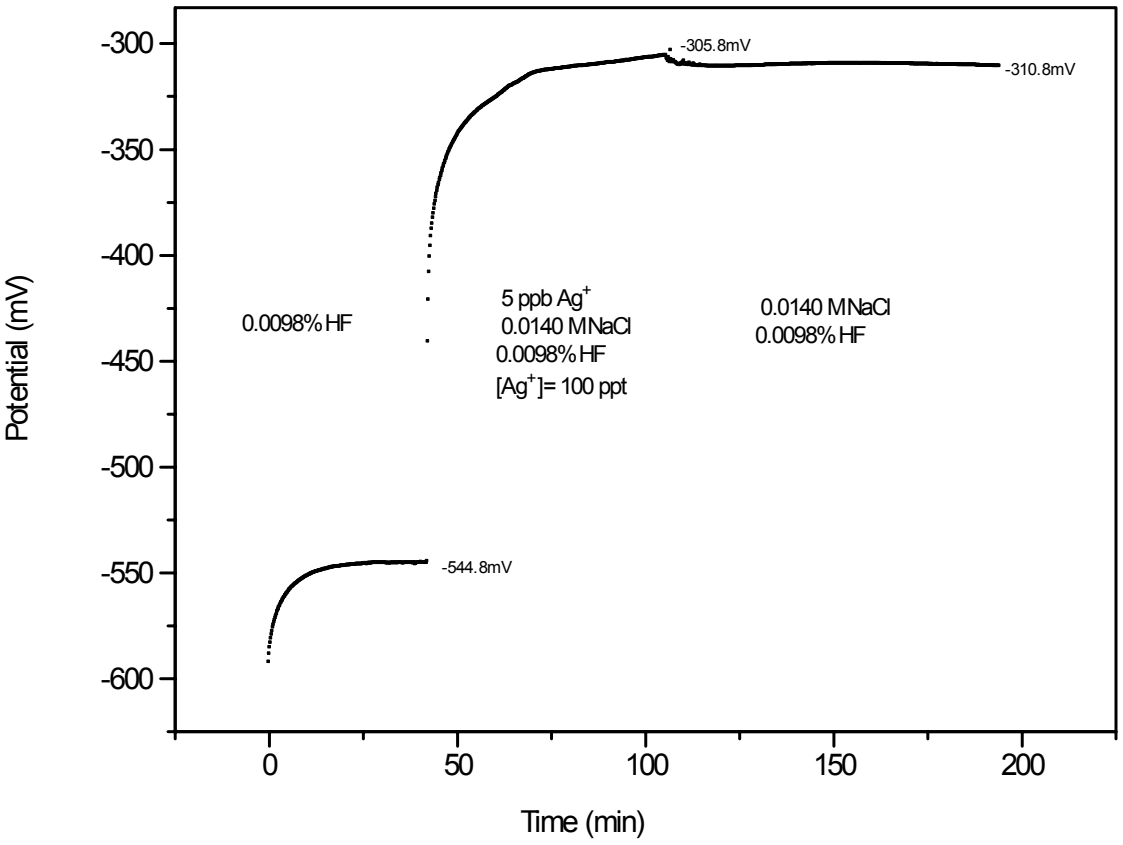


Figure 2.10: The open circuit potential measurement of 5 ppb Ag^+ with 0.014M NaCl in 0.0098% HF, transferred to 0.014M NaCl in 0.0098% HF

The heights of the second jumps of different concentrations but same complex ion with 5 ppb Ag^+ are studied within a certain rang, the height of the second jump is not dependent

on the complex ion's concentration within a certain range. In 5 ppb Ag^+ with 0.00206M, 0.0334M and 0.1M NaCl in 0.0098% HF, the ionic silver concentrations of these solutions are 100 ppt, 25 ppt and 3.3 ppt based on the MINEQL simulation results. The heights of the second jumps range from 40 to 50 mV 30 minutes after the sensor is transferred to fresh 0.0098% HF. The same phenomena are observed in Br^- and $S_2O_3^{2-}$. The heights of the second jumps of 5 ppb Ag^+ with 0.00206M, and 0.0334M NaCl in 0.0098% HF are shown in F igure 2.11. This is due to the high complex anion concentration and low silver concentration, the silver complex concentrations in these three solutions are not supposed to have big differences.

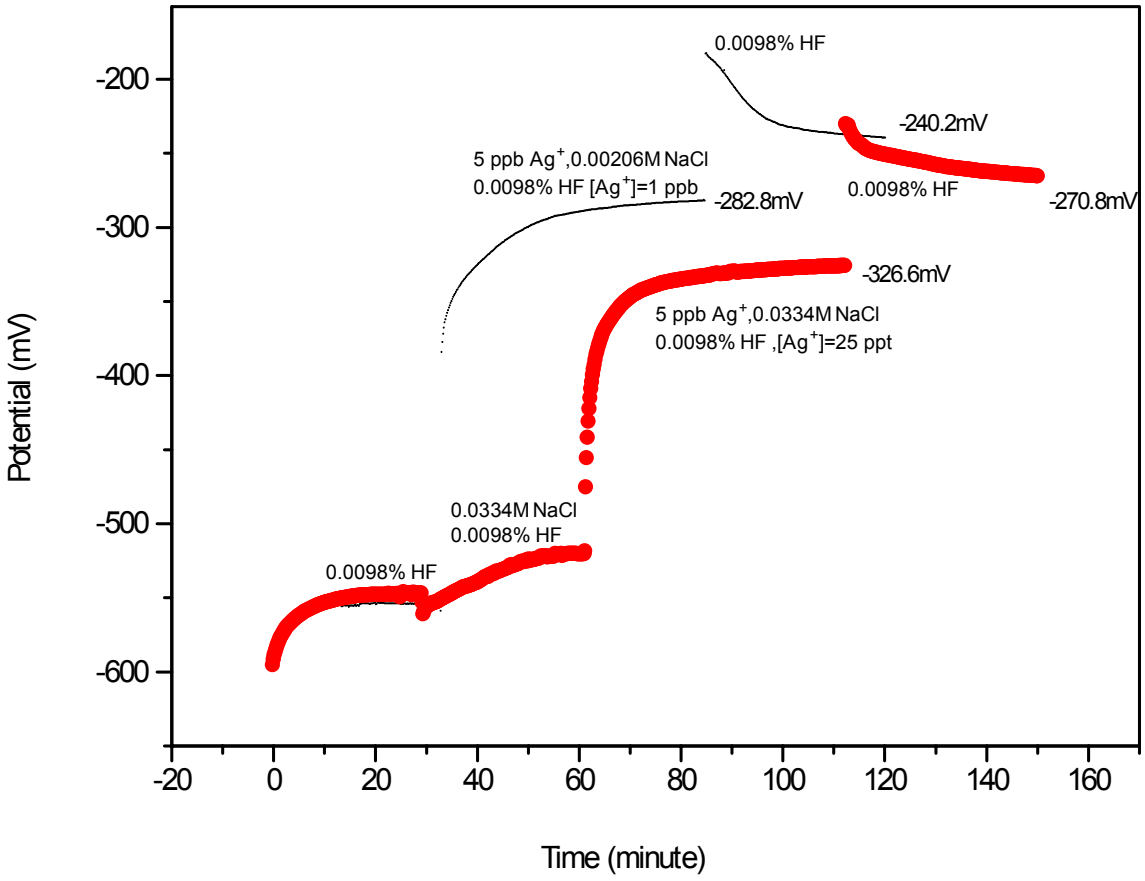


Figure 2. 11: The second jumps of 5 ppb Ag^+ with 0.0334 M and 0.00206 M NaCl in 0.0098 %HF

2.3.3.4 The relationship between complex formation constant and height of second jump

The second jump comes from the decomposition of the complex species absorbed on the surface of the silicon sensor. The stability of complex species is an important factor controlling the second jump signal. Cl^-, Br^-, $S_2O_3^{2-}$ and CN^- are all able to form complex with ionic silver, the formation constants are listed in Table 2.1: [24]

Ligand	Log K_1	LogK_2	LogK_3	LogK_4
Cl^-	3.04	5.04		5.30
Br^-	4.38	7.33	8.00	8.73
$S_2O_3^{2-}$	8.82	13.46		
CN^-		21.7	21.7	20.6

Table 2.1: The silver complex cumulative formation constants

The formation constant of these four species are increasing from Cl^- to CN^-, correspondingly, the heights of second jump decrease from Cl^- to CN^- as Figure 2.9,2.12 ,2.13 and 2.14 show:

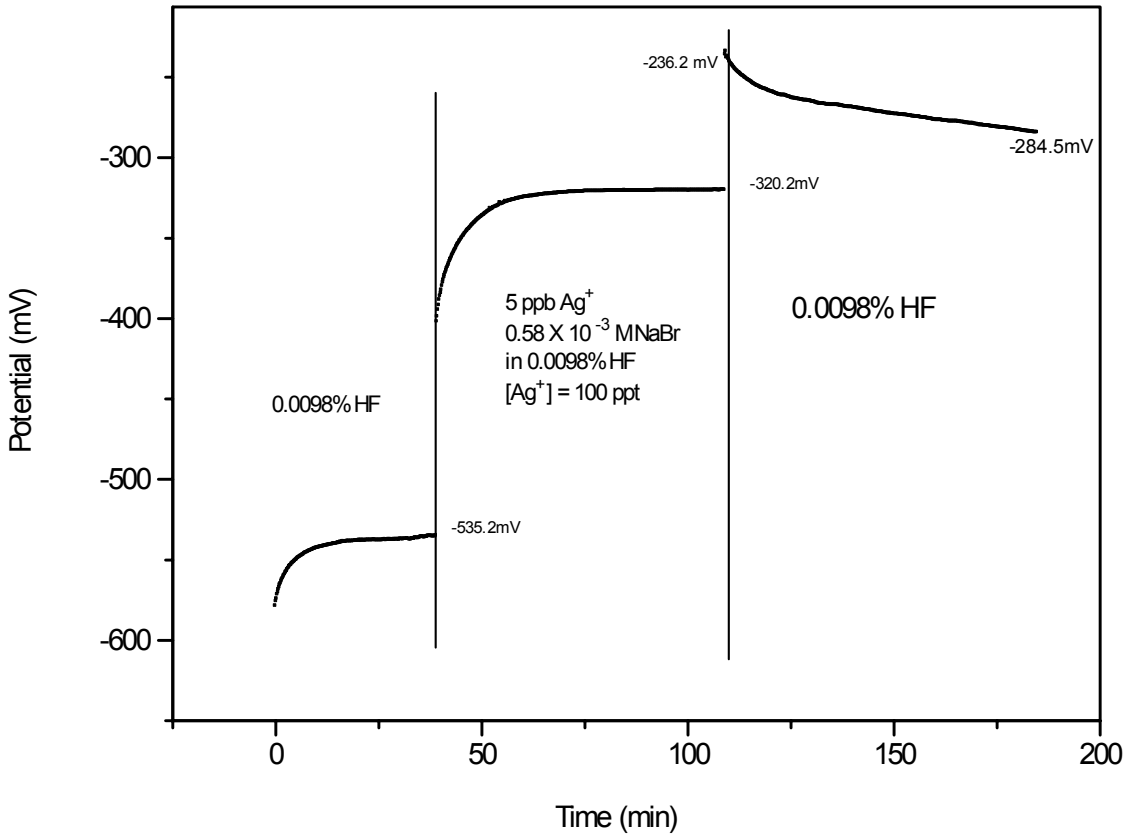


Figure 2.12: The open circuit measurement of 5 ppb Ag^+, 0.00058M NaBr in 0.0098 % HF

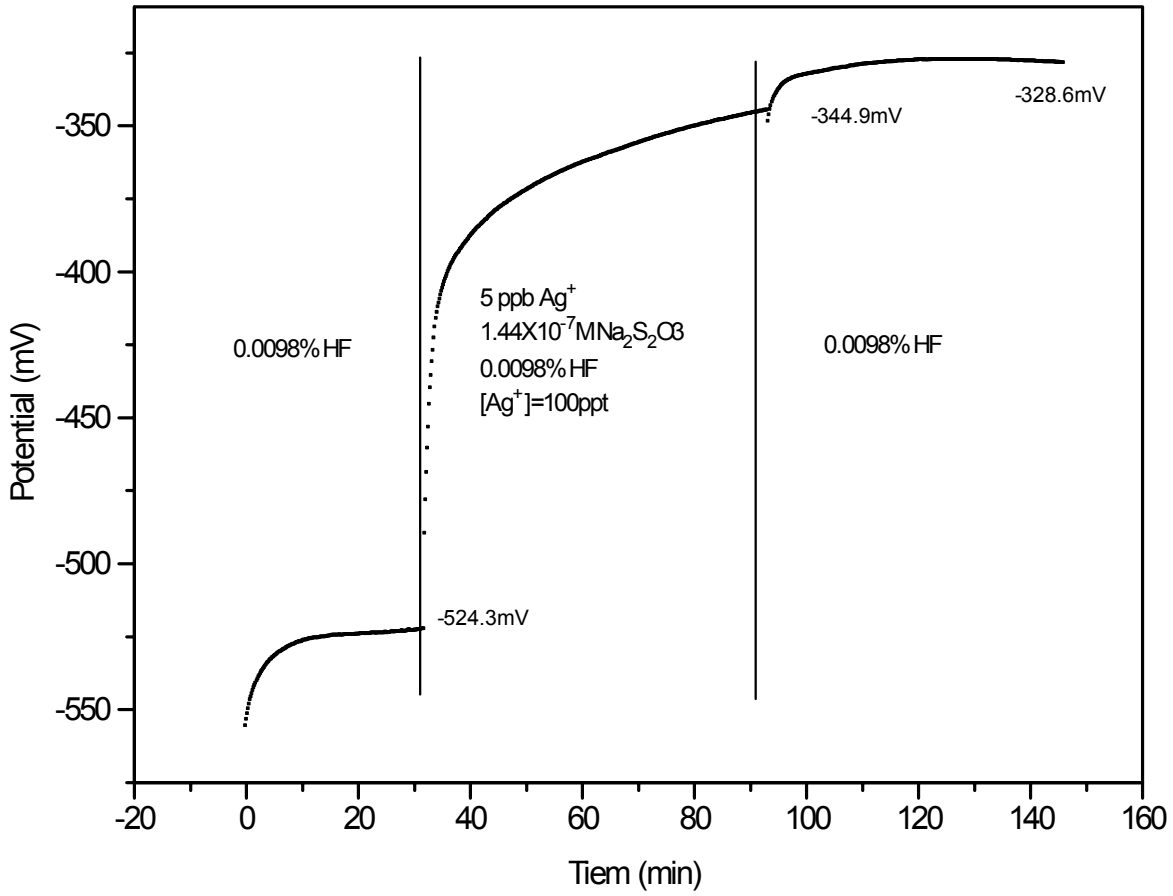


Figure 2. 13: OCP measurement of 5 ppb Ag^+, 1.44x10^{-7} M $Na_2S_2O_3$ in 0.0098 % HF

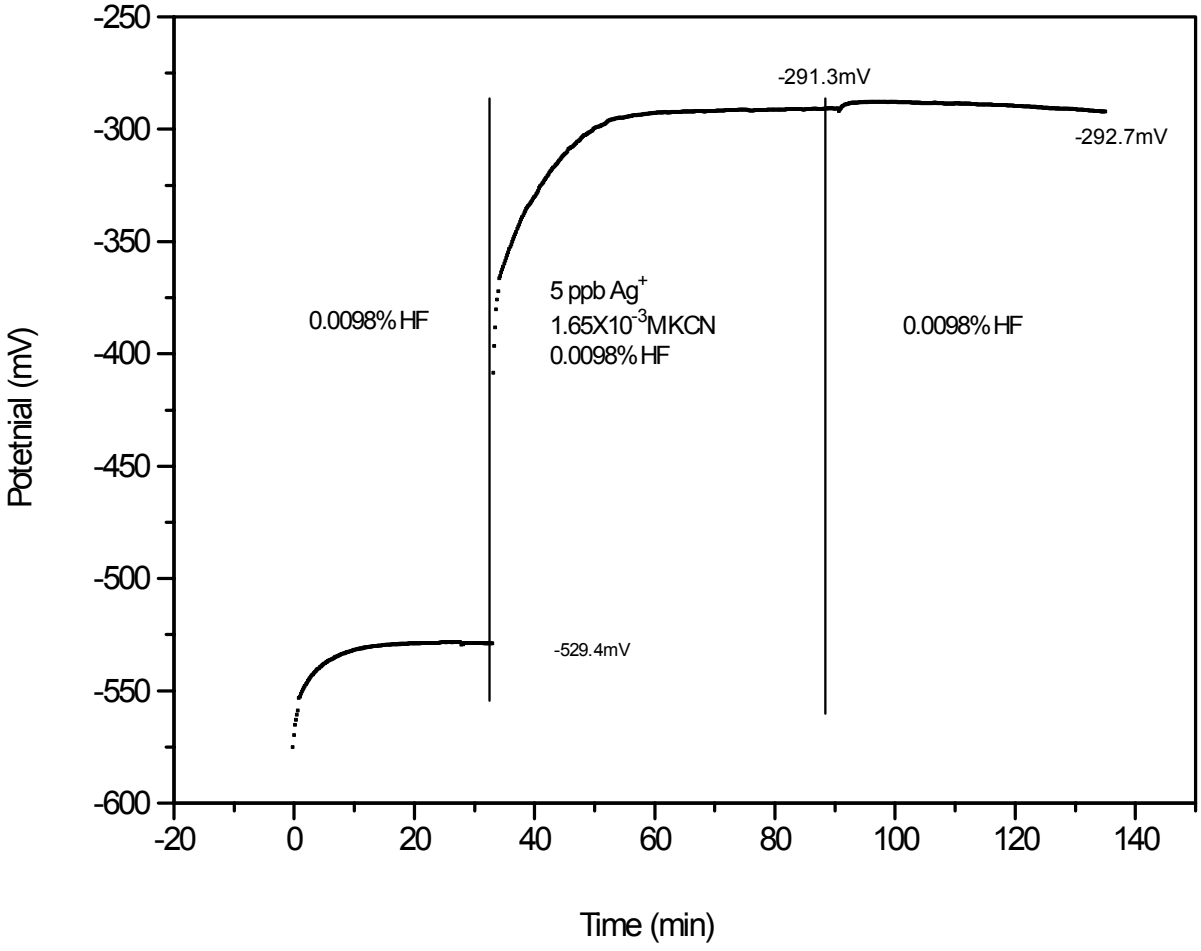


Figure 2.14: Open circuit measurement of 5 ppb Ag^{+}, 0.00165 M KCN in 0.0098% HF

The MINEQL simulation results show that the ionic silver concentrations are 100 ppt in 5 ppb Ag^+ with 0.014M NaCl, 0.00058M NaBr, $1.44x10^{-7}$ M $Na_2S_2O_3$, $1.65x10^{-3}$ M KCN in 0.0098 % HF solutions. But the OCP jumps are different, the second jumps are decreasing from Cl^- to CN^- as table 2 shows.

Species	Solution	$[Ag^+]$ *	Height of 2nd jump	1st formation const (Log K_1)
Cl^-	5 ppb Ag^+, 0.014M NaCl 0.0098% HF	100 ppt	53.7mV	3.04
Br^-	5 ppb Ag^+, 5.8e-4 M NaBr 0.0098% HF	100 ppt	35.7mV	4.38
$S_2O_3^{2-}$	5 ppb Ag^+, 1.44e-7M $Na_2S_2O_3$ 0.0098% HF	100 ppt	16.3mV	8.82
CN^-	5 ppb Ag^+, 1.65e-3 M KCN 0.0098% HF	12 ppt	1.4mV	21.0

*** the concentration is the MINEQL simulation result**

Table 2.2: Second jumps comparison among Cl^-, Br^-, $S_2O_3^{2-}$ and CN^-

From Cl^- to CN^-, the height of second jump drops from 53.7mV to 1.4 mV, it clearly correlates to the stability of these complexes. The results correspond to the formation constants of these complex species well.

CHAPTER 3

THE SILICON BASED SENSOR IN TOXICITY TEST

3.1 introduction

Silver is one of the most toxic heavy metals surpassed only by mercury, it is assigned to the highest toxicity class with cadmium, chromium copper and mercury.[26] Annual silver released to the environment from industry is about 2,500 tons, of which 150 tons become sludge of wastewater treatment plants, 80 tons are released to surface water .[26] The research of silver toxicity is surprisingly late, it began about 25 years ago. [27] Considerable progress has been made in the last a few years in the toxicity and bioavailability of silver to fish.[27] Now it is well documented that the toxicity of silver in the fresh water depends on the concentration of active free silver ion .[26] In fish, ionic silver binds to specific sites on the fish gills. Active uptake of sodium and chloride ions is reduced, primarily through the inhibition of Na^+, K^+-ATPase activities, causing the loss of ions from the blood plasma, circulatory failure through collapse of fluid volume regulation, and death of the fishes.[28] But in seawater, the mechanism is not so well understood. It is supposed that intestine is the primary toxic site of action and it is found out that acute toxicity of silver is much lower in seawater than in fresh water, it is estimated that it could be up to three orders magnitude less.[11] The reduced toxicity effect in seawater results partly from the different site of toxic effect. But more importantly it is from the fact that ionic silver is bound by the high concentrations of chloride ion in the seawater. [11]

The complex agent effect poses a difficulty in the research in the silver toxicity because people have to know the conditions of the complex agents and real concentration ionic silver in the water. And unfortunately the traditional analysis method such as Atomic Absorbance Spectroscopy(AAS) can't tell the difference between free ionic silver and silver complexes. Another difficulty is the unavailability of detection method of the low concentration ppt ionic silver that is more relevant in the environment. [11]

The silicon based sensor we discuss in chapter 2 has outstanding ability to overcome the above two difficulties. In nature environment, the typical silver concentration is at hundred part per trillion range.[8] As we have introduced in chapter 2, the silicon based sensor has high confidence to detect down to 50 ppt ionic silver in 0.0098% HF solution. In addition, this sensor is sensitive to ionic silver only but AAS can only give a total silver concentration based on its operation principle. The complex agent effect of the silicon based sensor is similar to the complex agent effect in the toxicity because the complex agent lowers both the sensor signal and toxicity. In other words, the complex agent effect in toxicity can be reflected by the silicon based sensor and this makes the sensor a toxicity indicator.

Several kinds of organisms are commonly used in toxicity tests such as Ceriodaphnia dubia, daphnia magna, rainbow trout, fathead minnows etc. Ceriodaphnia dubia(C. dubia), a kind of organism that lives in small ponds and rock pools, has many characters make it easy and economical to culture in laboratory, it is relatively small and sensitive to chemicals, it has short life cycle, it is easy to handle in laboratory.[30] The toxicity of

silver to Ceriodubia dubia is studied by some researchers.[35],[36] The hardness, pH value, alkalinity, complex agent effect are extensively studied. It is well accepted that the greater hardness will decrease the toxicity, increasing pH and alkalinity will result in less toxicity.[37] But there is a conflict about the complex agent Chloride 's effect. Russell J. Erickson [31]et al proposed that the chloride ion will increase the toxicity because of the neutral AgCl is more toxic than ionic silver, but some other researchers don't agree with this. Galvez and Wood [32] observe large consistent decrease of silver toxicity with addition of chloride. It is reported that the Silver LC 50 of 96 hours to Ceriodaphnia dubia in laboratory is 920 ppt, the range is 690 ppt to 1230 ppt with 95% confidence interval , the silver source used is silver nitrate.[31] Another author report the LC 50 of silver to C. dubia is 790 $\pm$ 180 ppt .[36] Silver thiosulfate is a highly soluble compound and main component of wastewater of photoprocessor with very low toxicity, it is 15,000-17,000 times less toxic than silver nitrate.[26] In this chapter we use sodium thiosulfate as a complexing agent to study the silver toxicity to Ceriodaphnia dubia, compare the toxicity data with the silicon based sensor data and MINEQL simulations.

3.2 Experiments

3.2.1 The open circuit potential measurement

The pretreatment of silicon sensor and measurement of silver solution is as chapter 2.2 describes. All the solutions for the toxicity test don't have any HF. They are prepared without HF and toxicity tests are performed(details will be introduced in following sections), then add HF to make them be 0.0098% HF solutions and make OCP measurements.

3.2.2 The toxicity tests

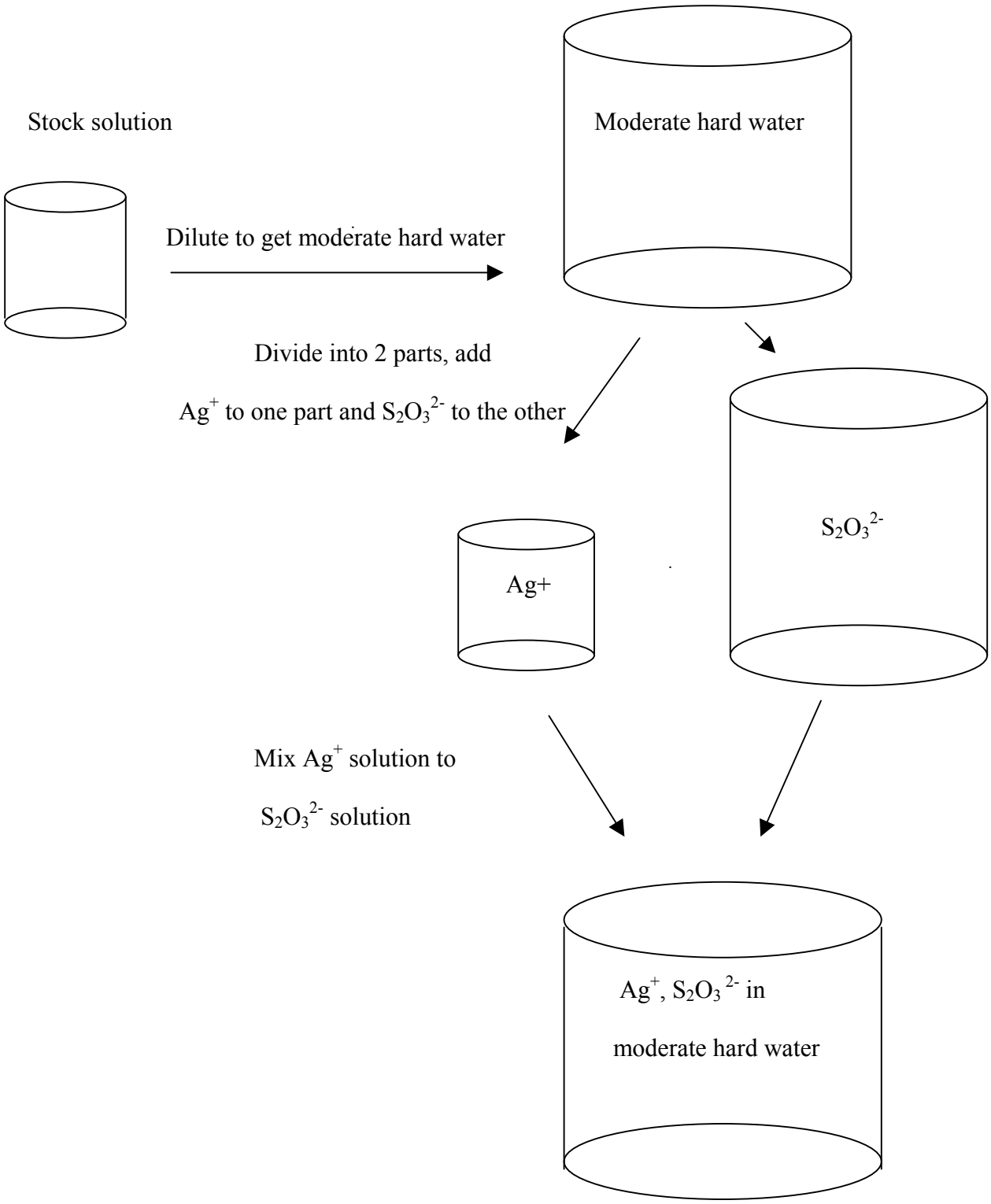
3.2.2.1 The Ceriodaphnia dubia organism

All the C.dubia organisms are from Department of Environmental Science lab, University of North Texas. All the organisms in tests are less than 1 day old for young C. dubia are more sensitive to chemicals. All the organism are cultured in chamber with constant temperature 25 degree centigrade.

3.2.2.2 The preparation of silver thiosulfate solution and chemicals, equipment

Strategy must be taken to avoid the decomposition of sodium thiosulfate and reduction of silver ions which can happen if high concentration silver solution is added to sodium thiosulfate solution. The first step is to make moderate hard water, the composition is 4 ppm KCl 96 ppm $NaHCO_3$, 60 ppm $MgSO_4$, 60 ppm $CaSO_4.2H_2O$.[34] Then distribute a part of this moderate hard water to two bottles and, add thiosulfate stock solution to one part of solution and add silver stock solution to the other part. Both silver and thiosulfate solutions are diluted before they mix together. Slowly pour the silver solution into the thiosulfate solution, mix well.

The silver and thiosulfate additions are done 30 minutes before the toxicity tests. The procedure of making the solution is illustrated in scheme 3.1. After the solutions are mixed well, they are brought into chamber for temperature equilibrium for about 20 minutes. Then the solutions are distributed to 50 ml condiment cups, each cup contains 15 ml solutions. Ceriodaphnia dubia with culture media are transferred by dropper to the condiment cup made from polystyrene material. Mortality in each cup is observed and recorded in 24 hours and 48 hours. The pH value, hardness, alkalinity, temperature, dissolve Oxygen and are measured according to EPA standard methods [33] after the solutions are prepared.



Scheme 3.1: The steps of making silver thiosulfate solution

Sodium bicarbonate and sodium thiosulfate are from EM science; Potassium chloride, analytical reagent, is purchased from Mallinckrodt chemical works; $MgSO_4.7H_2O$ is from J.T. INC; $CaSO_4 .2H_2O$ is from Fisher scientific. Equipment includes Orion 520 pH meter, YSI model33 S-C-T meter, YSI model 51B Oxygen meter. Silver solution is from diluted from 10,000 silver ICP/DCP standard solution, Aldrich chemical.

3.3 Results and discussions

3.3.1 The toxicity of silver in moderate hard water to Ceriodaphnia dubia

The toxicity of silver in moderate hard water is tested, the concentrations of Ag^+ are 0 ppt, 50 ppt, 100 ppt, 200 ppt, 400 ppt, 800 ppt, 1600 ppt. All the solutions distributed in 5 condiment cups, each cup contain 15 ml solution of each kind and 4 Ceriodaphnia dubias, solutions are kept static all the time, and temperature is constant at 25 degree centigrade in the chamber. At the end of first 24 hours and 48 hours the survival rate of the C. dubia is checked and recorded, the results are listed in table 3.1 :

Solution Number	Ag^+ [ppt]	survival rate (24 h)		survival rate(48 h)	
		alive/total	percentage	alive/total	percentage
1	0	15/15	100%	14/15	93%
2	50	15/15	100%	15/15	100%
3	100	15/15	100%	15/15	100%
4	200	15/15	100%	15/15	100%
5	400	14/15	93%	12/15	80%
6	800	9/15	60%	4/15	27%
7	1600	14/15	93%	0/15	0%

Table 3.1 The toxicity ionic silver in moderate hard water to C. dubia

The solution No. 1 is moderate hard water, it does not have any toxicity to C. dubia throughout 48 hours, and 50 ppt, 100 ppt, 200 ppt don't show significant toxicity to C. dubia at 24 hours and 48 hours as table 3.1 shows. At the concentration of 400 ppt Ag^+, only one of 15 C. dubias is dead at 24 hours and 3 of 15 are dead at 48 hours. At the end

of 48 hours, 11 of 15 C. dubias are dead in the 800 ppt silver solution and 15 of 15 are dead in the 1600 ppt silver solution.

EPA probit analysis program,[38], [39] a statistical analysis program, is used to calculate the silver lethal concentration to C. dubia in moderate hard water. The calculation result is listed in table 3.2. The LC/EC 50 of silver in moderate hard water to C. dubia is 599.539 ppt as table 3.2 shows. This value is comparable to the literature value 920 ppt [31] and 790 ppt.[36]

Point	Concentration(ppt)	Lower (ppt)	Higher(ppt)
LC/EC 1.00	232.679	79.516	339.914
LC/EC 5.00	307.017	137.681	414.614
LC/EC 10.00	355.924	183.487	463.150
LC/EC 15.00	393.264	222.059	500.758
LC/EC 50.00	599.539	459.672	753.699
LC/EC 80.00	914.008	731.123	1476.406
LC/EC 90.00	1009.897	794.081	2361.643
LC/EC 99.00	1544.816	1090.754	4071.369

Table 3.2 The silver lethal concentration to C. dubia in M.H.W.

The alkalinity, pH value, conductivity, dissolved oxygen are measured using EPA standard methods all the solutions don't have abnormal value. Table 3.3 lists all these data.

PARAMETER	UNIT	VALUE
Dissolved oxygen	**mg/L**	**10.3~10.4**
pH	**N/A**	**7.60-7.81**
hardenss	**mg/L as $CaCO_3$**	**60~70**
alkalinity	**mg/L as $CaCO_3$**	**55~65**
conductivity	**μmhos/cm**	**245~265**

Table 3.3 Water characteristics for water used in toxicity tests

Corresponding to the toxicity tests, the open circuit potential measurements are done in ionic silver in moderate hard water, 0.0098% HF. The calibrations curve is shown in Figure 3.1. At the LC 50 concentration 599 ppt, the sensor response is about –350 ~-340mV, we propose this potential be the lethal potential of the silicon sensor to C. dubia, if the signal from the silicon sensor is higher than –350~-340mV, at the end of 48 hours we will observe significant toxicity to C. dubia .

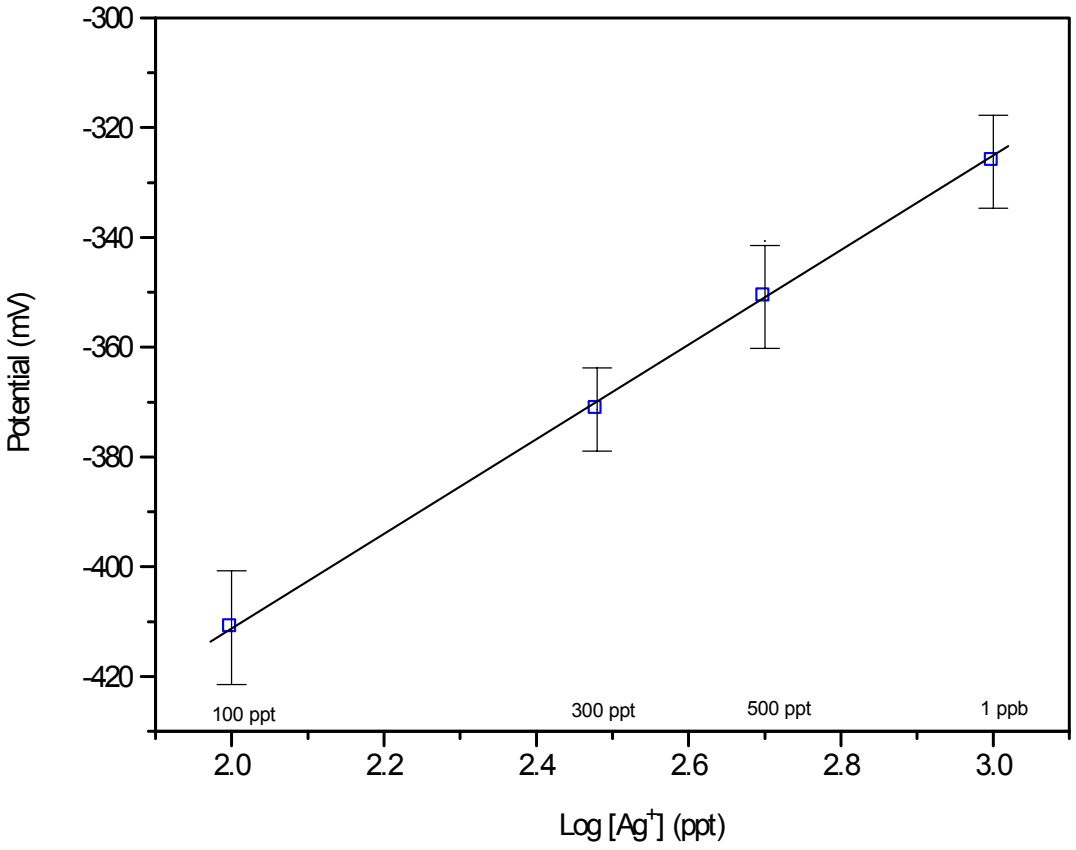


Figure 3.1: The calibration curve of silver in moderate hard water, 0.0098% HF

A linear regression equation for the calibration curve is available from the Figure 3.1:

$$\mathbf{Y = -582.0 + 85.3\ X}$$

Y: Potential

X: $Log[Ag^+]$

R = 0.99978 , SD = 0.91338, N = 4, P = 0.00022

3. 3. 2 The toxicity of sodium thiosulfate to Ceriodaphnia dubia

It is necessary to understand the toxicity of sodium thiosulafte 's toxicity to C. dubia before we can study its complex effect on the silver's toxicity to C. dubia.

A series concentrations, $9.3x10^{-7}$ M, $9.3x10^{-4}$ M, $9.3x10^{-3}$ M Sodium thiosulfate in moderate hard water are prepared and toxicity tests are performed as chapter 3.3.1 describes. The Table 3.4 is the test data.

Solution No.	Concentration(M) ($Na_2S_2O_3$)	Survival rate(24h)		Survival rate(48h)	
		Alive/total	percentage	Alive/total	percentage
1	0	19/21	90%	18/21	86%
2	$9.3X10^{-7}$	20/21	95%	20/21	95%
3	$9.3X10^{-4}$	21/21	100%	20/21	95%
4	$9.3X10^{-3}$	12/16	75%	8/16	50%

Table 3.4 The toxicity of sodium thiosulfate in moderate hard water to C. dubia

In Table 3.3, we find that in moderate hard water, from concentration $9.3x10^{-7}$M to $9.3x10^{-4}$ M, sodium thiosulfate is safe to C. dubia up to 48 hours. At the concentration of $9.3x10^{-3}$, 50 percent C. dubia are dead in 48 hours, it indicates this concentration or higher should be avoided to used in the silver toxicity studies.

3.3.3 The complexing effect on the silver toxicity to Ceriodaphnia dubia

3.3.3.1 The toxicity test based on the MINEQL simulation

When we talk about the complex effect on the open circuit potential measurement of silver with sodium chloride and sodium thiosulfate in 0.0098% HF solution in chapter 2, we find out that the OCP signal is much higher than it should be based on the MINEQL simulation. And, we propose that the MINEQL simulation is unreliable at ppt low concentrations.

In this chapter, section 3.3.1 gives us a very good biosensor to test the reliability of the MINEQL simulation and compare with the silicon based sensor signal. We use C. dubia as biosensor here, and prepare the silver with sodium thiosulfate in moderate hard water solution for the toxicity tests. The ionic silver concentrations in these solutions are given by the MINEQL simulation and we know from section 3.3.1 that at this specified ionic silver concnetration, less than 400 ppt within 48 hours, the C. dubia must be safe. The toxicity result will judge the conflict between MINEQL simulation and silicon sensor.

Based on the MINEQL simulation Figure 3.2, in the 10 ppb Ag^+, $9.3x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water, the ionic silver concentration is 25 ppt and in 10 ppb Ag^+, $0.8x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water solution, the ionic silver concentration is 2 ppb.

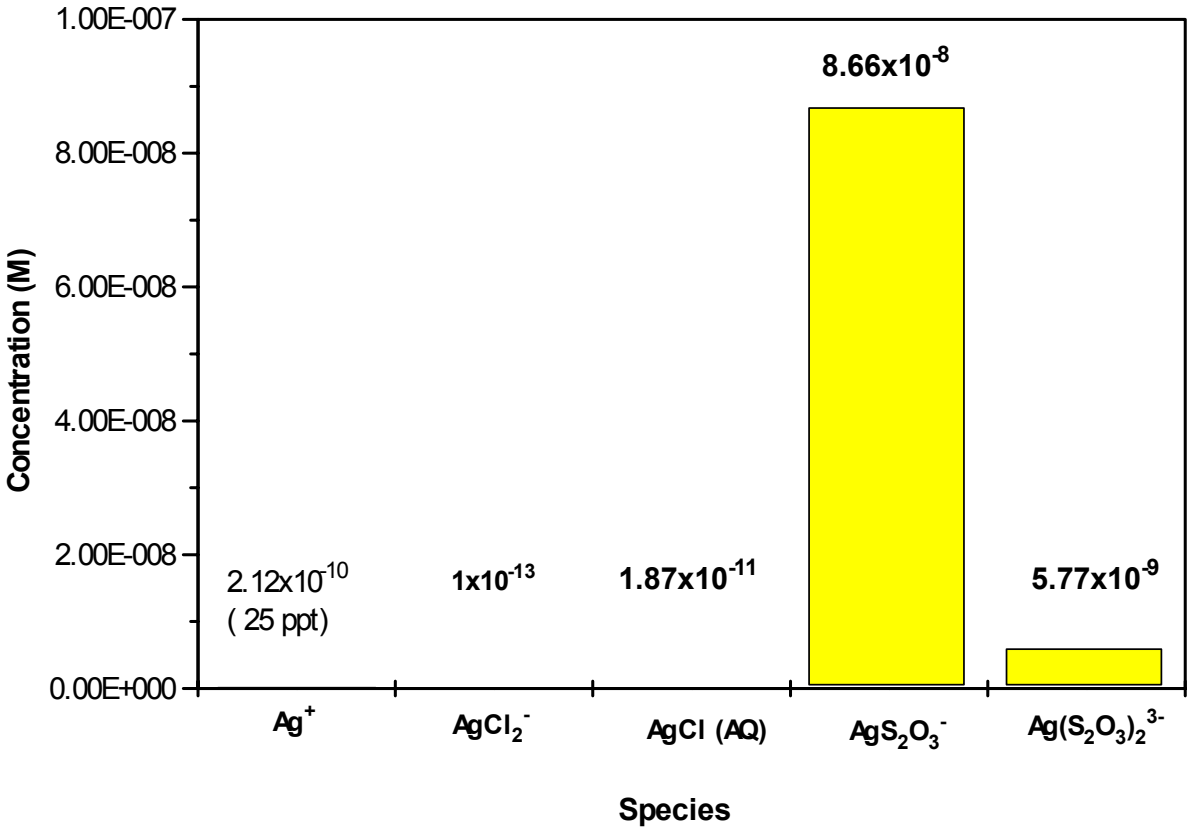


Figure 3.2: The MINEQL simulation of 10 ppb Ag^+, $9.3x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water $[Ag^+]$=25 ppt ;

A series of silver solutions without or with sodium thiosulfate solutions are prepared, the ionic silver concentrations are given by MINEQL for solutions with $Na_2S_2O_3$ and the ionic silver concentrations of solutions without $Na_2S_2O_3$ are given by the preparation process. Toxicity tests to C. dubia are listed in Table 3.5.

Solution	Composition	$[Ag^+]$	Survival ate(24h)	survival ate(48h)
1	Moderate hard water	0 ppt	100%	100%
2	10 ppb Ag^+ ,$9.3x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water	25ppt*	0%	0%
3	25 ppt Ag^+ in moderate hard	25 ppt	100%	100%
4	10 ppb Ag^+,$0.8x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water	2ppb*	0%	0%
5	2 ppb Ag^+ in moderate hard water	2 ppb	0%	0%
6	10 ppb Ag^+ in moderate hard water	10 ppb	0%	0%

Table 3.5 The toxicity tests of silver with sodium thiosulfate in moderate hard water based on the Mineql simulations

*** MINEQL simulation result**

In solution No. 2 in the Table 3.5, the free ionic silver concentration is 25 ppt based on the MINEQL simulation. According to the toxicity result we have in section 3.3.1, 25 ppt ionic silver is safe to C. dubia within 48 hours and section 3.3.2 already proved to us that the $9.3x10^{-7}$ Mol/L sodium thiosulfate is safe to C. dubia within 48 hours. But Table 3.5 shows the C. dubias in this solution are all dead at the end of 48 hours. The solution No.3 , 25 ppt Ag^+ in moderate hard water, confirms that the 25 ppt ionic silver does not have any acute toxicity to C. dubia within 48 hours. This toxicity result conflicts with the MINEQL simulation. The ionic silver concentration must be higher than 25 ppt to kill C. dubia. It is not surprise that in solution No. 4, 5,6 the C. dubia are all dead because of the higher ionic silver concentration.

Besides the above toxicity tests, we also use the silicon based sensor to measure the open circuit potential of the solutions in interest. We add HF solution to 5 ppb Ag^+, $9.3x10^{-7}$ M $Na_2S_2O_3$ in moderate hard water solution and measure the OCP signal. The Ksp of AgOH is $2x10^{-8}$, this solution doesn't have AgOH , adding H^+ ion will increase the acidity of the solution but will not change the ionic silver concentration. F^- is not a good complexing agent with silver, it won't affect the ionic silver concentration significantly either. Figur3.3 is the MINEQL simulation of 10 ppb Silver, $9.3x10^{-7}$ M $Na_2S_2O_3$, 0.0098%HF in moderate hard water, compare with Figure 3.2, it is found that the Ag^+ concentration change slightly after adding HF.

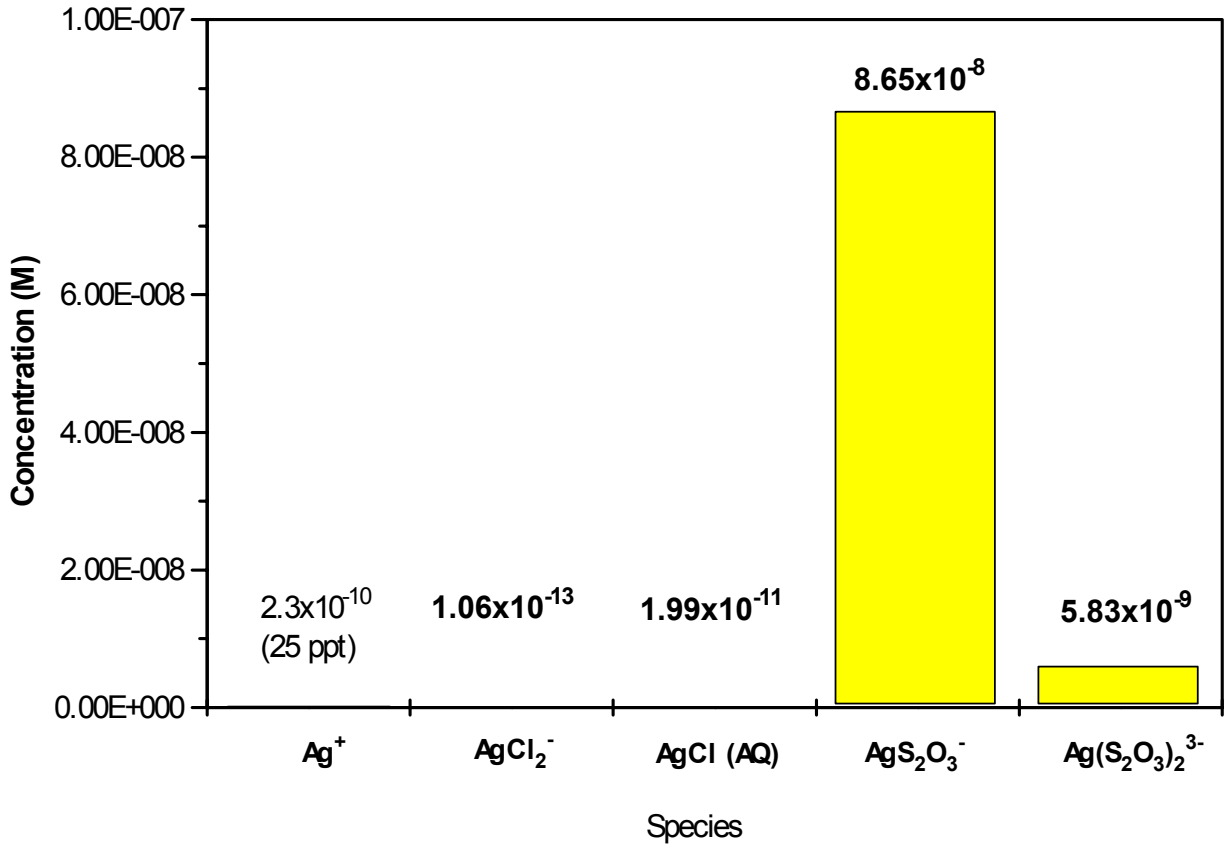


Figure 3.3 : The MINEQL simulation of 10 ppb Ag^{+}, 9.3x10^{-7} M $Na_2S_2O_3$,0.0098% HF in moderate hard water

The open circuit potential measurement of the silicon sensor with in the 10 ppb Ag^+, $9.3x10^{-7}$ M $Na_2S_2O_3$, 0.0098% HF in moderate hard water is shown in Figure 3.4.

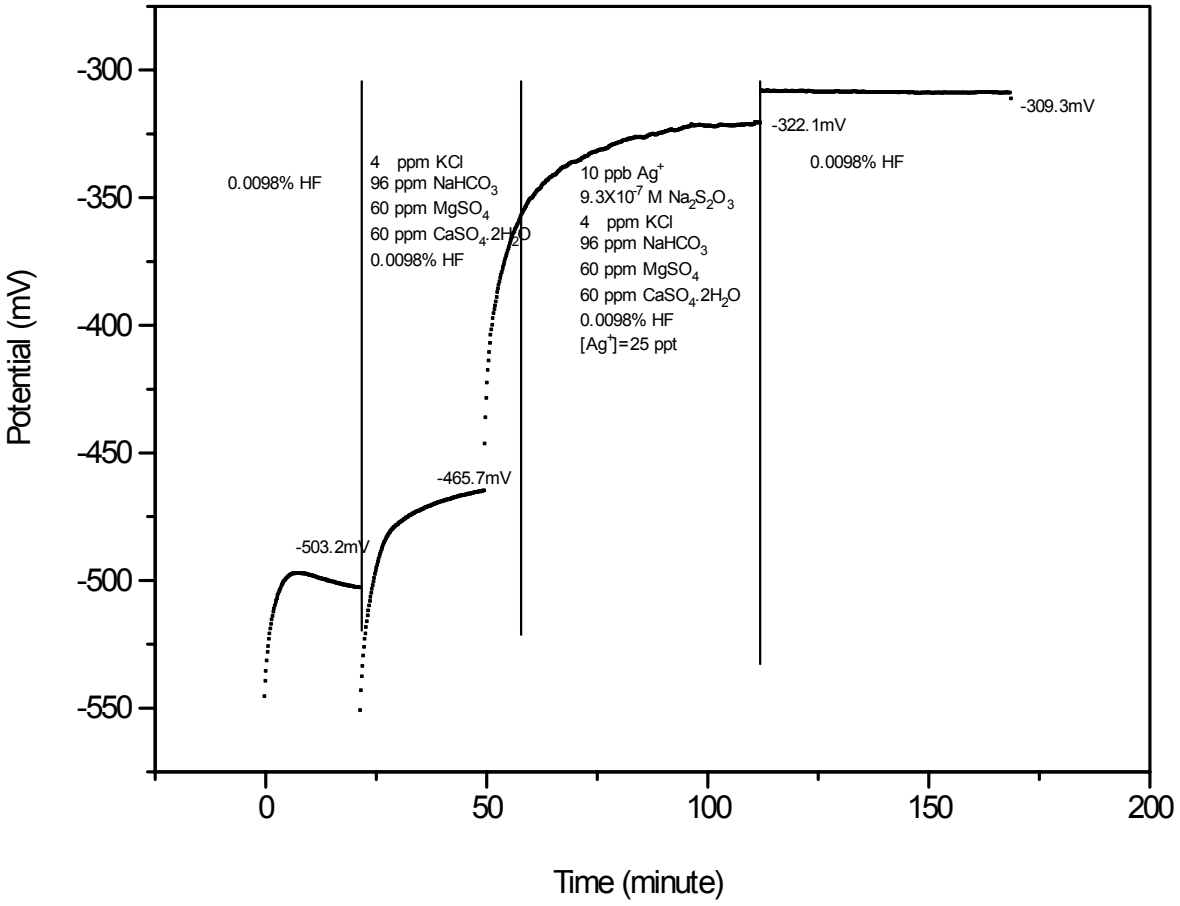


Figure 3.4: The OCP measurement of silicon sensor in 10 ppb Ag^+, $9.3x10^{-7}$ M $Na_2S_2O_3$, 0.0098% HF, in moderate hard water

Figure 3.4 shows that the open circuit potential jump is –322.1 mV, this jump is much higher than that of 25 ppt silver solution and it must be in at ppb range. This indicates the sensor doesn't show the ionic silver's concentration is 25 ppt, it is much higher than 25 ppt. The toxicity test also indicates that the ionic silver concentration must be higher than 25 ppt because in this solution all the C. dubia are dead. It also obeys the conclusion we make in section 3.3.1, when the OCP measurement is higher than –350 mV, the silver solution has acute toxic to C. dubia. The biosensor C. dubia and silicon based sensor correspond to each other well but both conflict with the MINEQL simulation.

3.3.3.2 The toxicity tests based on silicon sensor OCP measurement

It turns out that 9.3×10^{-7} M $Na_2S_2O_3$ in 0.0098% HF solution, whose ionic silver concentration is 25 ppt based on MINEQL simulation, is not enough to suppress the toxicity of 10 ppb ionic silver to Ceriodaphnia dubia in moderate hard water, and the silicon sensor open circuit potential measurement of silicon sensor also confirms this. But we understand that sodium thiosulfate is able to suppress the ionic silver concentration. We can use silicon sensor to detect concentration of ionic silver, and try to correlate the toxicity results to the ionic silver concentration based on silicon sensor measurement result since we failed to correlate toxicity result with MINEQL result.

A series of 10 ppb Ag^+ in sodium thiosulfate solutions with increasing sodium thiosulfate concentrations in moderate hard water are prepared. The correspondence between the toxicity of these solutions to C. dubia within 48 hours and open circuit potential

measurement of the silicon based sensor are studied. These solutions are 10 ppb silver with 9.3 $x10^{-7}$, $9.3x10^{-6}$, $9.3x10^{-5}$, $9.3x10^{-4}$, $9.3x10^{-3}$ $9.3x10^{-2}$ M sodium thiosulfate in moderate hard water, the toxicity tests results are listed in Table 3.6.

Solution No.	$Na_2S_2O_3$ Concentration.(M)	Survival rate(24h)		Survival rate(48h)	
		Alive/total	percentage	Alive/total	percentage
1	0	20/20	100%	20/20	100%
2	$9.3x10^{-7}$	0/20	0%	0/20	0%
3	$9.3x10^{-6}$	19/20	95%	0/20	0%
4	$9.3x10^{-5}$	19/20	95%	17/20	85%
5	$9.3x10^{-4}$	20/20	100%	19/20	95%
6	$9.3x10^{-3}$	20/20	100%	10/20	50%
7	$9.3x10^{-2}$	0/20	0%	0/20	0%

Table 3.6: The $Na_2S_2O_3$ concentration effect on the toxicity of 10 ppb silver to C. dubia in moderate hard water

In section 3.3.2, we already study the toxicity effect from the sodium thiosulfate itself and conclude that when the sodium thiosulfate concentration is higher or equal than $9.3x10^{-3}$ M, it begins to have acute toxicity to daphnia under out experiment conditions. It is understandable that in solution No.7 in Table 3.6 all the C. dubia are all dead, this can be due to the toxicity from the sodium thiosulfate. The solution No. 6 has 50% survival rate, it is same as we get in solution No.4 in Table 3.3 which has same sodium thiosulfate concentration $9.3x10^{-3}$ M but without any silver. This suggests that the silver has been complexed to non-toxic lever by sodium thiosulfate and the sodium thiosulfate is responsible for the death of C. dubia.

In solution No. 5 in Table 3.6, the sodium thiosulfate concentration is $9.3x10^{-4}$ M, the 19 out of 20 C. dubia survive after 48 hours. This results indicates that 10 ppb silver ions is mostly complexed by thiosulfate down to non toxic level, and $9.3x10^{-4}$ M $Na_2S_2O_3$ does not have acute toxicity to C. dubia within 48 hours, this also confirms the previous study. The solution No. 4 which has $9.3x10^{-5}$ M $Na_2S_2O_3$, 17 out of 20 C. dubia are alive at the end of 48 hours, it also indicates that the silver is mostly complexed to non toxic level. The solution No. 3 and No.2 when the $Na_2S_2O_3$ concentrations are $9.3x10^{-6}$ and $9.3x10^{-7}$ M, all C. dubia are dead. It indicates that the silver is not complexed enough to be safe level to C. dubia. But the MINEQL simulation result conflicts with this experiment fact, we have talked about this in section 3.3.2.

These solutions in Table 3.6, after adding HF to make 0.0098% HF, are measured by silicon sensor to get open circuit potential signal. The results are compared with the toxicity results and MINEQL simulations. The OCP signals of these solutions are shown in Figure 3. 5.

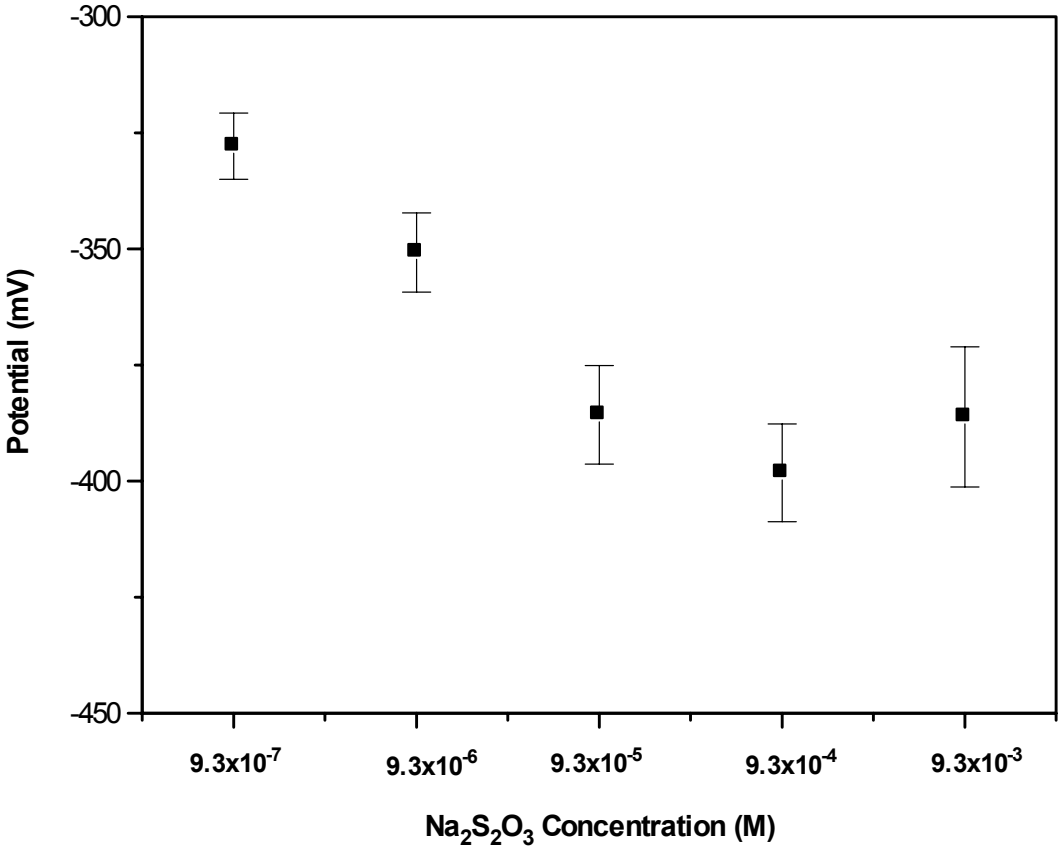


Figure 3.5: The OCP signal of 10 ppb Ag^+, $9.3x10^{-7}$, $9.3x10^{-6}$, $9.3x10^{-5}$, $9.3x10^{-4}$, $9.3x10^{-3}$ M $Na_2S_2O_3$ in moderate hard water, 0.0098% HF

These open circuit potential measurement signals are put into the equation we got in section 3.3.1:

$$\mathbf{Y = -582.0 + 85.3\ X} \quad (\text{ Y: Potential X: Log}[Ag^+]\text{ })$$

The concentrations can be easily calculated and the results are compared with the simulation results and toxicity results in Table 3.7.

Total silver Conc. (ppb)	**$Na_2S_2O_3$ Conc.(M)**	**Ionic[Ag^+]from simulation(ppt)**	**OCP (mV)**	**Ionic [Ag^+] from Si sensor measurement(ppt)**	**C.dubia survival rate**
0	**0**	**0**	**N/A**	**0**	**100%**
10	**$9.3x10^{-7}$**	**25**	**-327.8**	**912~1698**	**0%**
10	**$9.3x10^{-6}$**	**1.3**	**-355.7**	**347~645**	**0%**
10	**$9.3x10^{-5}$**	**$2.6x10^{-2}$**	**-385.7**	**123~229**	**85%**
10	**$9.3x10^{-4}$**	**$2.9x10^{-4}$**	**-409.3**	**55~102**	**95%**

Table 3.7 Comparison of ionic [Ag^+] from simulation and from OCP measurement, and C. dubia survival rate

Table 3.7 clearly shows that the discrepancy between the simulation ionic silver concentration and measured ionic silver concentration .In 10 ppb silver with $9.3x10^{-7}$ M

$Na_2S_2O_3$, simulation gives 25 ppt and OCP measurement gives the 912~1689 ppt. If the simulation is right the C. dubia survival rate should be close to 100%, but 0% is alive. This survival rate is reasonable to the silicon sensor OCP measurement result 912~1698 ppt. That the survival rate is 0% confirms the OCP measurement of the silicon sensor and conflicts with the simulation. When the sodium thiosulfate concentration is $9.3x10^{-6}$ M, the silicon sensor measurement gives the ionic silver concentration 347~645 ppt , and all C. dubia are dead. This indicates a small discrepancy between biosensor and silicon sensor because at this concentration range, there should be some C. dubias alive.

CHAPTER 4

CONCLUSION

It is clearly demonstrated in previous chapters that the silicon based sensor is able to detect trace level ionic silver in 0.0098% HF. A calibration curve of open circuit potential versus silver concentration logarithm from 50 part per trillion to 10 part per billion silver is available. The complex agent has significant effect in lowering the open circuit potential signal for complexing the ionic silver in 0.0098% hydrofluoric acid. Different complex agents have different ability to lower the silicon sensor OCP signal because of different formation constants of complex.

When the complex agent is used to the silver solution, the complex adsorbed on the surface of the silicon sensor will decompose and release ionic silver and cause the second OCP jump when the sensor is transferred to fresh 0.0098% hydrofluoric acid. The height of the second OCP jump is the complex formation constant dependent. Higher formation constant complex causes lower OCP jump. The MINEQL chemical equilibrium modeling software is used to simulate the distribution of the species in the silver and complex solution, the ionic silver concentration in the solution is available from the simulation. A discrepancy between simulation concentration and OCP measurement is found. The ionic silver concentration resulted from the OCP measurement is found to be higher than the MINEQL simulation concentration.

The toxicity of ionic silver to C. dubia is studied the LC50 within 48 hours is found to be 599 part per trillion. Corresponding to the toxicity of ionic silver, the silicon sensor OCP measurement of the silver solution is compared with the toxicity of silver. The silicon sensor OCP measurement of the sensor could be a toxicity indicator. Also corresponding to the complex agent effect to the OCP measurement of the silver, a similar complex agent effect to the silver toxicity is found. The complex agent can effectively lower the silver toxicity to C. dubia. MINEQL simulation, again, is used to simulate the ionic silver concentration in the solution. A discrepancy is found between the simulation result and the toxicity to biosensor C. dubia result. The toxicity study result indicates the ionic silver concentration is higher than the MINEQL simulation concentration. The silicon based sensor OCP measurement and toxicity result support each other and both are not in agreement with the MINEQL simulation.

Furthermore, when more complex agent thiosulafte than the simulation is added to the suppress the ionic silver concentration and get lower silicon sensor OCP signal, the toxicity of silver can be correspondingly suppressed. The OCP measurement of silicon sensor and toxicity result, again, support each other and are against the MINEQL simulation. In addition, it clearly demonstrates that the silver thiosulfate comlex is much less toxic to C. dubia than ionic silver. This is proven in the toxicity comparison experiments between 10 part per billion silver with 9.3×10^{-7} M $Na_2S_2O_3$ solution and 10 part per billion silver with 9.3×10^{-4} M $Na_2S_2O_3$ solution. The latter has higher complex concentration and lower ionic silver concentration but is less toxic.

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